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THE UNDEAD

VOLUME 1

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ENAT SCIENCE

THE UNDEAD

FIRST ADDITION

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PREFACE

THIS BOOK IS FOR SECOND YEAR UNIVERSITY STUDIENTS TAKING CHEMISTRY AND CHEMISTRY RELATED PRACTICALS. IT PROVIDES WITH THE REFRENCE NEEDED BY THE STUDIENT BEFORE ATAMPTING TO WRITE HIS PRACTICAL WRITE UP. IT WAS WRITTEN ASSUMING FIRST YEAR CHEMISTRY PRACTICAL EXPIRIANCE. THIS BOOK CONTAINS TIPICAL PRACTICALS IN ORGANIC CHEMISTRY, INSTRUMENTAL AND SPECTROSCOPIC METHODS OF ANALYSIS, MAIN GROUD AND TRANSITION METALS CHEMISTRY.

CONTENTS

LAB REPORT FORMAT 5
ORGANIC CHEMISTRY 9
SAPONIFICATION 9
PINACOLE PINACOLONE 14
Sythesis of anthranilic acid 20
benzilic rearangements 25
ENDOLE SYNTHESIS 32
sythesis of anthraqinone 37
instrumental and spectroscopic methods of analyisis 43
flame atomic absobtion spectroscopy 43
detemination of hardness of water 43
FLAME ATOMIC EMISSION SPECTROSCOPY 52
Determination of sodium in drinking water 52
UV VIS SPECTROSCOPY 59
Coulorimetric determination of Phosphorus in Cola Drinks 59
Characterization of quinine and its determination 68
MAIN GROUP AND TRANSITION METALS CHEMISTRY 77
REACTION OF COPPER 77
d block elements – manganese 86
d block elements chromium 95
d block elements iron 104
THANK YOU 114

LAB REPORT FORMAT

The lab report is an essential component of any experiment, both as a method of communicating the importance of your work, and as a way to allow others to repeat your work. The point of the experiment, i.e. the theory motivating it and the insights that may be gleaned from it should be immediately clear. Procedures and methods must be described in such a way that a second person can repeat the experiment and analysis of it using the report alone.

General Comments

1) Length is not equal to quality. Be clear and concise. Be sure to clearly define any terms or symbols that you use in your report.
2) Write the report as if for a classmate who has a similar chemical background but has not taken this class. Explain what you did and what it means.
3) Reports should be typewritten. Requirements: Font size: 12, Theme Font: Times New Roman, spacing: 1.5 (Equations or calculations may be ***neatly*** hand written).
4) Make the report readable. Use the spelling and grammar checkers and make sure the document is properly formatted, i.e. consistent use of fonts, text alignment, etc.
5) Any figure, table, spectrum or computer output must be labelled with a number, and should be referred to by that number in the text of the report. (Look at any journal article to see examples of this).
6) Always make sure you have included in your lab report anything that is explicitly asked for in the practical schedule. Failure to do this will result in loss of points.
Reports must be submitted on or before the day of the next practical. Late submission will not be accepted and you will not be allowed to perform the next experiment.
The report must consist of the following items/subsections:

1) Cover Sheet

- Your name and registration number
- Your partners' name(s)
- Date experiment was done
- Title for the experiment (as given in the lab hand-out) and experiment number.
- Abstract - Important results and conclusions (e.g. we determined that our unknown solvent was… or …the surface tension of methanol is…)

2) Theory

This section should be brief but should put the experiment in context. ***DO NOT PLAIGARISE!*** Everything should be in your own words otherwise expect penalties.

It must include:

- A summary of the theoretical principles of the experiment.
- The kind of information that can be gained
- How the information is obtained (a ***brief*** mention of the method or technique being used – include any relevant references)
- How the results of the experiment may be useful (what information can we get from the measured parameters?)
- Any other information relevant to the experiment in question

3) Procedure

- **Apparatus and Materials:** (include a figure of the set up if appropriate).
- A brief but clear outline of the working methods so that the experiment may be repeated from your report without reference to another manual.
- It should be in point form
- All statements should be impersonal. **DO NOT** say "I took a 50ml beaker" **BUT RATHER SAY** "A 50 ml beaker was taken" etc.
- Describe completely and in detail any changes to the referenced procedure.
- State the number of runs and the conditions of the experiment (e.g. temperature, pressure).
- Include the names and makes/models of any equipment that you used in the measurement of your data.

4) Results

- **Tabulations of data and results from the calculations:** Include a title and clearly label columns with defined parameters and units. Fix the number of significant figures reported by a spreadsheet program.
- **Spectra:** Include a title and label the axes with units. Spectrometer settings (number of scans etc.) and other relevant details (such as temperature or pressure) should be included in the Procedure.

5) Calculations/Analysis

- **Graphs:** Include a descriptive title, label both axes and include units. If the graph includes data and a best fit to an equation, be sure that there is a correctly labelled legend explaining the symbols used. Display the equation used to fit the data.
- **Sample calculations:** Include an easy to follow sample of each one of your calculations.

6) **Discussion**

• Critically assess your experimental accuracy and precision. How might these be improved? Identify possible sources of error along with the effects these may have had on your results.

• Assess agreement with other literature values, and discuss your results in relation to the literature errors, i.e. do the results agree within the listed uncertainties. Don't forget the references.

• Assess the validity of any theory.

• Finally, always remember to address any questions posed in the practical schedule, but do so in a manner consistent with your discussion.

7) Conclusion

Answer your aims/objectives and all important results.

8) References

Note references with superscripts within the text, and include the bibliography at the end of your report using the **American Chemical Society** style:

Journal

Lastname1, A. B.; Lastname2, C. D.; Lastname, E. F. Title of Article. *Journal Abbreviation* **Year**, *Volume*, Inclusive Pagination.

Park, M.V.D.Z.; Neigh A. M.; Vermeulen, J. P.; De la Fonteyne, L.J.J.; Verharen, H. W.; Briedé, J. J.; Van Loveren, H.; De Jong, W. H. The effect of particle size on the cytotoxicity, inflammation, developmental toxicity and genotoxicity of silver nanoparticles. *Biomaterials* **2011**, *32*, 9810-9817.

Book

Lastname1, A. B.; Lastname2, C. D.; Lastname, E. F. *Book Title*, Edition Number (if applicable); Series Information (if any); Publisher: Place of Publication, Year; Volume Number (if applicable), Pagination.

Atkins, P.; de Paula, J. *Physical Chemistry*, 8th Edition; Oxford University Press: Oxford, 2006; p 200.

Levine, I. N. *Physical Chemistry*, 6th Edition; Mcgraw-Hill: New York, 2009; Chapter 2.

Shakhashiri, B. Z. *Chemical Demonstrations: A Handbook for Teachers of Chemistry*; The University of Wisconsin Press: Madison, 1983; Vol. 1, Chapter 2.

Internet Sources

Lastname1, A. B. (if any); Lastname2, C. D.; Lastname, E. F. Title of Site. URL (accessed date), other identifying information.

Olsen, A. Burning Calories: How Much Energy is Stored in Different Types of Food? http://www.sciencebuddies.org/science-fair-projects/project_ideas/FoodSci_p012.shtml (accessed January 2014).

University of Zimbabwe Library Home Page. http://www.library.uz.ac.zw (accessed March 2014).

9) Answers to Questions.

Always make sure you answer all questions. Failure to do this will result in loss of marks.

ORGANIC CHEMISTRY

SAPONIFICATION

NAME

REG NUMBER

PROGRAMME

PRACTICAL DATE

PRACTICAL NUMBER

TITLE **Saponification**

AIMS AND OBJECTIVES -to produce soap from pure cooking oil (soya bean).

-to measure the weight of manufactured soap .

-to observe the texture and colour of manufactured soap

THEORY

When a fatty acid, mainly a vegetable oil or animal fat in the soap handmade process, comme into contact with a base (soda or lye), it occurs a chemical reaction named saponification. The result of the saponification is two by-products generaly named soap and glycerin (glycerol). Actualy, at the origin, the soap was a combination of these two by-products.Soap made with “Noddle process” or “Hot saponification process” needs several weeks to dry and to be hard meanwhile with the “Cold saponification process” soap is hard after 30/40 seconds. The production capacity of « Noddle process » or « Hot S. process » are unlimited meanwhile the « Cold saponification soap » is rare. The cold process uses just enough heat to ensure that all the fat is melted prior to reacting it with the base. Preferably the cold process is simpler, requires less time and energy, while resulting in a creamier bar. The hot process uses heat to speed the reaction resulting in fully saponified soap by the time you pour your soap into moulds. (Kemp,1967)

Vegetable oils and animal fats are the main materials that are saponified. These greasy materials, triesters called triglycerides, are mixtures derived from diverse fatty acids. Triglycerides can be converted to soap in either a one- or a two-step process. In the traditional one-step process, the triglyceride is treated with a strong base (e.g., lye, which accelerates cleavage of the ester bond and releases the fatty acid salt and glycerol. This process is the main industrial method for producing glycerol. If necessary, soaps may be precipitated by salting it out with saturated sodium chloride. The saponification value is the amount of base required to saponify a fat sample. For soap making, the triglycerides are highly purified, but saponification includes other base hydrolysis of unpurified triglycerides, for example, the conversion of the fat of a corpse into adipocere, often called "grave wax." This process is more common where the amount of fatty tissue is high, the agents of decomposition are absent or only minutely present. (Adams, 1974)

Sunflower is an example of vegetable oil used to manufacture soap .Sunflower oil is a mono un saturated fattty acid and poly un saturated fatty acids mixture of mostly oleic acid omega 9, linoleic acid (omega 6).Sunflower oil contains aliphatic hydrocarbons terpene and methyl ketons.The constituents of sunflower oil are palmitic acid 4-9%, steanic acid 1-7%, oleic acid 14-40%, linoleic acid 48-74%. Soaps are less effective in hard water, which is water that contains a significant concentration of Mg^{2+} and Ca^{2+} ions. These ions form precipitates with soap molecules, and this precipitate is often seen as a gray line on a bathtub or sink and is often called “soap scum”. Since soap forms a precipitate with these ions, it means that many of the soap molecules are no longer present in the solution. Therefore, soap will form fewer suds in hard water“Soft water” is water that contains very few or no ions that precipitate with soap. Soap will therefore be much more effective in soft water than in hard water. (Lehman, 1981)

Reaction of triglycedride with NaOH

(Loudon, 1995)

The melting point of a fat depends on the amount of unsaturation in the fatty acids. Fats with a preponderance of unsaturated fatty acids have melting points below room temperature and are called oils. Fats with little un-saturation are solids at room temperatures. For the manufacture of soaps and for certain food uses, solid fats are preferable to oils. The melting point of a natural fat may be increased by hydrogenation. Industrially, the process is called hardening. Vegetable oils such as cotton seed and peanut are often hardened to the consistency of lard by partial hydrogenation. (Vogel, 1952)

PROCEDURE.

In to a 1000ml beaker,140 ml of delight soya bean oil fat were measured using a measuring cylinder.20g of NaOH were measured using a balance and were dissolved into 40ml of distilled water in a beaker until the solution dissolved. The measured 140ml of plant oil was heated in the beaker to 90º, then the hot caustic soda was added drop wise to the hot oil while stirring in an anticlockwise direction also maintaining the temperature in the range 70º-80º.The mixture was stirred thoroughly until the caustic soda was finished and up until the mixture gelatinised into a thick porridge.lt was then poured into a mould, insulated and left to react overnight.

RESULTS

Weight of soap	157g
Soap colour	Cream
Texture	Hard
Ph	neutral

CALCULATIONS

% yield =(157\160)*100

=98.125

DISSICUSION

The soap that was produced was hard, and in theory this might have been contributed by the present of low unsaturation in the fatty acids present in the soya bean cooking oil. These fatty acids include oleic acid (14-40%) and linoleic acid (48-74%).The hardness of the soap should have been improved by a process called hardening. Hardening is the partial hydrogenation of fats or oils thus increasing the melting temperatures. Fats with little unsaturation are solid at room temperature, for the manufacture of soaps and for certain food users solid fats are preferable to oils. Soaps made with higher percentages of soft oils such as pure cooking oil will be harder and slower to un-mold , these soaps take much more time to set up and harden. The percentage yield was over 98%.

CONCLUSION

Weight of soap	-	157g
Soap colour	-	cream
Texture	_	hard
pH	_	Neutral
% yield	-	98%

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PINACOLE PINACOLONE

NAME

REG NUMBER

PROGRAMME

PRACTICAL DATE

PRACTICAL NUMBER

TITLE PINACOL PINALONE REARRANGEMENT

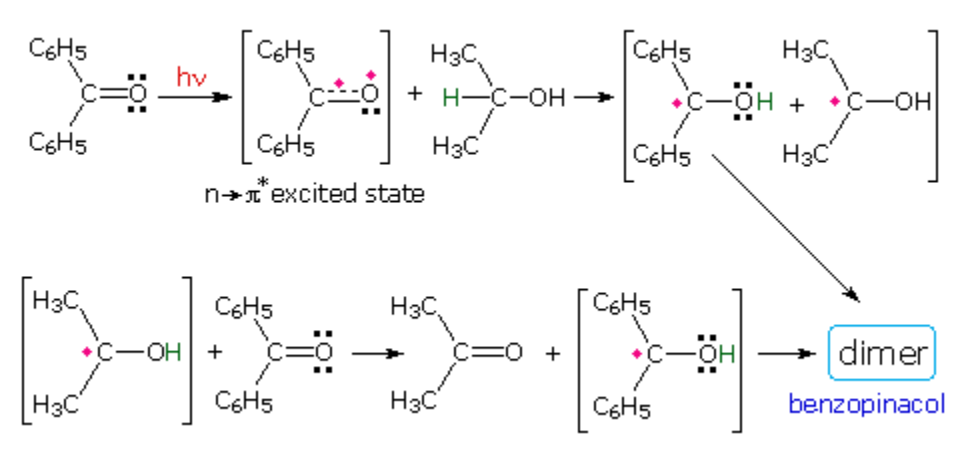
AIMS AND OBJECTIVES - : To produce benzolpinacol

To record the yields

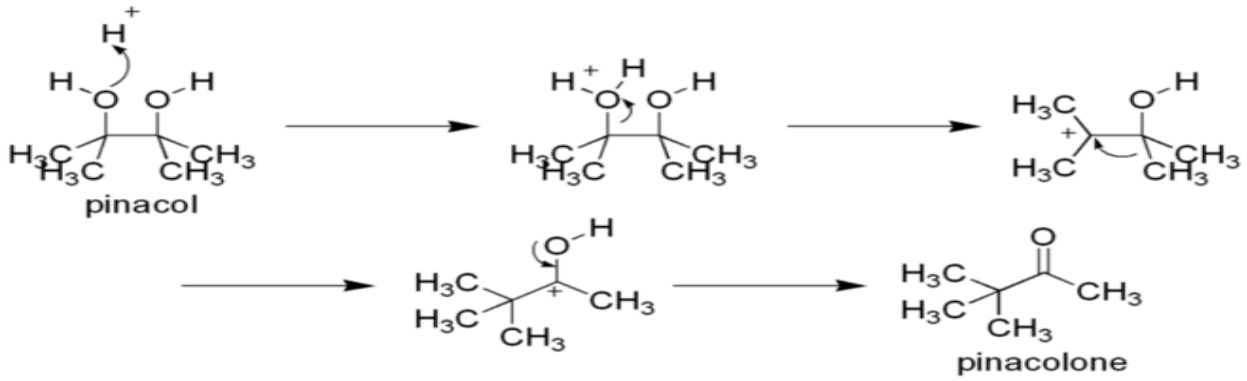
: To prepare benzolpinacolone

To record its melting point

MECHANISM



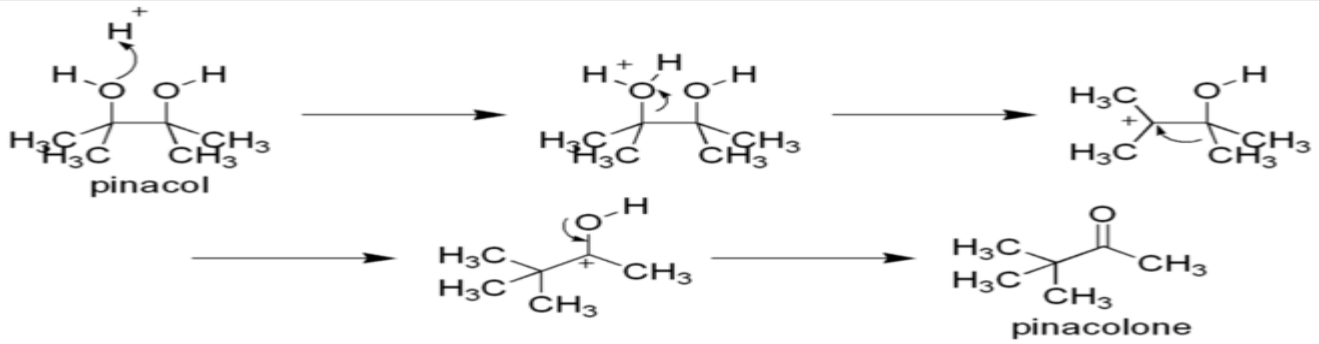
Synthesis of benzopinacol (Monson, 1971)



Synthesis of Benzopinacolone (Smith and March, 2007)

Theory

The **pinacol-pinacolone rearrangement** is a method for converting a 1,2-diol to a carbonyl compound in organic chemistry. The 1,2-rearrangement takes place under acidic conditions. The name of the rearrangement reaction comes from the rearrangement of pinacol to pinacolone.



This reaction was first described by Wilhelm Rudolph Fittig in 1860 of the famed Fittig reaction involving coupling of 2 aryl halides in presence of sodium metal in dry etherial (Kemp, 1967)

In the course of this organic reaction, protonation of one of the –OH groups occurs and a carbocation is formed. If both the –OH groups are not alike, then the one which yields a more stable carbocation participates in the reaction. Subsequently, an alkyl group from the adjacent carbon migrates to the carbocation center. The driving force for this rearrangement step is believed to be the relative stability of the resultant oxonium ion, which has complete octet configuration at all centers (as opposed to the preceding carbocation). The migration of alkyl groups in this reaction occurs in accordance with their usual migratory aptitude, i.e.hydride > Phenyl > tertiary carbocation (if formed by migration) > secondary carbocation (if formed by migration) > methyl cation . The conclusion which group stabilizes carbocation more effectively is migrated. (McMurry 1984)

In cyclic systems, the reaction presents more features of interest. In these reactions, the stereochemistry of the diol plays a crucial role in deciding the major product. An alkyl group which is situated trans- to the leaving –OH group alone may migrate. If otherwise, ring expansion occurs, i.e. the ring carbon itself migrates to the carbocation centre. This reveals another interesting feature of the reaction, viz. that it is largely concerted. There appears to be a connection between the migration origin and migration terminus throughout the reaction.Moreover, if the migrating alkyl group has a chiral center as its key atom, the configuration at this center is *retained* even after migration takes place. (Streitwiser 1976)

The **benzilic acid rearrangement** is the rearrangement reaction of benzil with potassium hydroxide. The reaction is a representative of 1,2-rearrangements. These rearrangements usually have migrating carbocations but this reaction is unusual because it involves a migrating carbanion. The long established reaction mechanism updated with silicone. (Streitwiser 1976)

A hydroxide anion attacks one of the ketone groups in in a nucleophilic addition to the hydroxyl anion . The next step requires a bond rotation to conformer which places the migrating group R in position for attack on the second carbonyl group in a concerted step with reversion of the hydroxyl group back to the carbonyl group. This sequence resembles a nucleophilic acyl substitution. Calculations show that when R is methyl the charge build-up on this group in the transition state can be as high as 0.22 and

that the methyl group is positioned between the central carbon carbon at a separation of 209 pm. (Loudon 1995)

Procedure (a)

A mass of 2.7 grams of benzolphenone was placed in a50ml round bottomed flask. A volume of 20 ml 2-propanol was added and desolved the solid by warming on steam bath. A volume of 1 drop glaicial acetic acid was added and 2-propanol was added to fill the flask. The flask was expose to sunlight for 5-6 days .the crystal were collected the yield was recorded

(b)

A mass of 1.5 benzopinacol was placed in 100 ml round bottomed flask. A volume of 8mls glacial acetic acid and a small crystal of iodine was added. The mixture was refluxed for 10 min. a volume of 8 mls ethanol was added angd stired and then allowed to cool. The crystals were collect by saction and the melting point recorded

Results

TABLE: WEIGHING OF BENZOLPINACOL

Mass of watch glass/g	43.20g
Mass of watch glass + sample/g	45.7
Mass of sample /g	2.5

TABLE: WEIGHING OF BENZOPINACOLONE

Mass of watch glass/g	43.20g
Mass of watch glass + sample/g	45.2
Mass of sample /g	1.8

CACULATIONS

Benzolpinacol

% yield = (mass of sample/ theoretical mass) * 100

=48 %

Mp 172 d.c

Benzopinacolone

% yield =(mass of sample/ theoretical mass)* 100

= 98%

MP 194 D.C

Discussion

The experiment went well and proceed ass expected but there are some problems. During the exposure of benzolpinacol to crystalize on the sunlight there was an overcast for the days so the amount of sunlight was very minimum. This affects the overall final yield of the benzol pinacol. This problem might be solved by exposing the round bottomed flask to artificial sunlight. The deviation from theoretical melting point arise from the contamination of the chemicals. These problem might be overcome by using clean apparatus all the time and using analytical grade chemicals. The vacuum pump was not working properly which cause the crystals to be a little moist which cause weight increase. This can be eliminated by using a new vacuum pump and washing crystals throughly.

Conclusion

Percentage yield of benzolpinacol 48

Mp 172

Percentage yield of benzolpinacolone 98

MP 194

Answers to question

1. A.
2. Iodine acts as a base and pulls out the hydrogen of the oxygen attached to the same carbon on which benzene is attached.
3. Benzilic acid and Benzopinacolone have almost the same melting point which ranges from 182 – 185℃
4. Glacial acetic acid (pure anhydrous acetic acid) is used as the reaction solvent, but it also plays an important role as an acid catalyst. the halogenation reaction requires the reactant ketone be tautomerized to the enol form, which occurs under acid catalysis (base catalysis on the other hand would yield the corresponding enolate anion). So as the I_2 consumes the enol form by reacting with it, more enol will need to be generated and the acetic acid increases the rate at which this happens, thereby accelerating the overall reaction. The tautomerization mechanism involves simply protonation of the carbonyl oxygen of the ketone followed by deprotonation of its alpha carbon (carbon adjacent to the carbonyl carbon), with replacement of the CO double bond with a single bond and the formation of a double bond between the carbonyl carbon and the alpha carbon. Glacial means water free

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SYTHESIS OF ANTHRANILIC ACID

NAME

REG NUMBER

PROGRAMME

PRACTICAL DATE

PRACTICAL NUMBER

TITLE Synthesis of ANTHRANILIC ACID

AIMS AND OBJECTIVES - : To produce anthranlic acid from

To record final yield

To compare theoretical melting point with the

The one obtained in the experiment

Theory

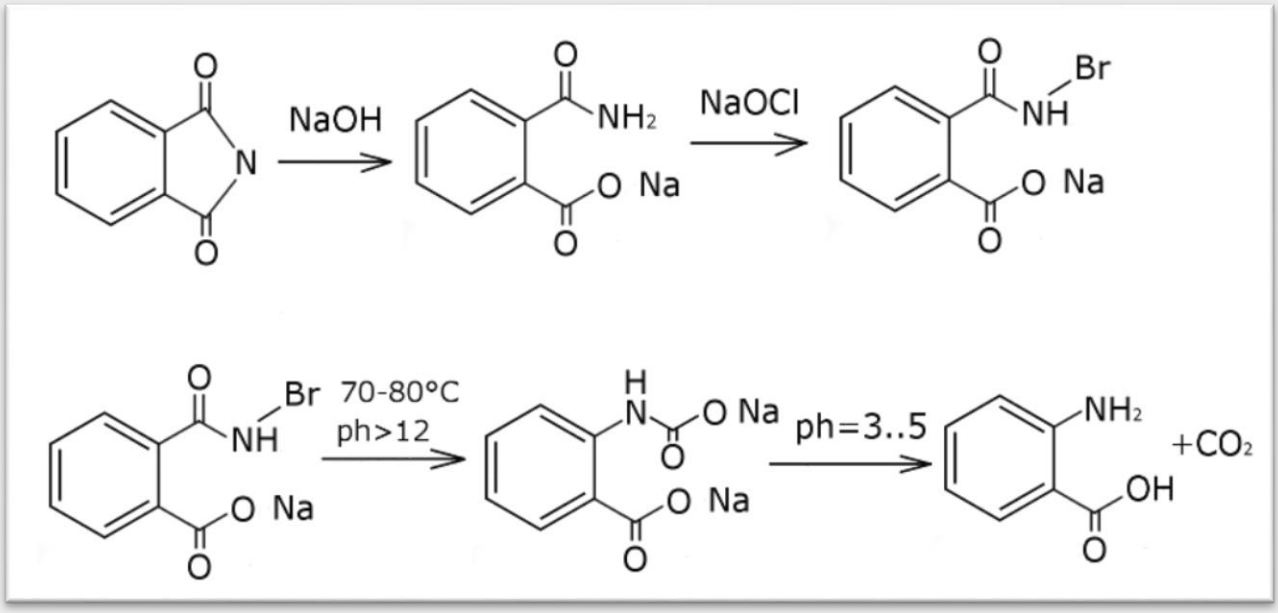
Anthranilic acid can be used in organic synthesis to generate the benzyne intermediate. It is used as an intermediate for production of dyes, pigments, and saccharin. It and its esters are used in preparing perfumes to imitate jasmine and orange, pharmaceuticals and UV-absorber as well as corrosion inhibitors for metals and mold inhibitors in soya sauce.(McMurry, 1984)

Several investigators worked on the synthesis of anthranilic acid dyes in the various conditions which have shown significant biological activity especially against bacteria S. aureus and E. coli. The mixed ligand complexes of Co (II), Ni (II), Cu (II) and Zn (II) with anthranillic acid and tributylphosphine have shown profound activity against Staphylococcus, (Streitwiser, 1976)

Anthranilic acid (o-amino-benzoic acid, 2-aminobenzoic acid, 2-AA, 2AA, AA) is an aromatic acid with the formula $C_6H_4(NH_2)(CO_2H)$. The molecule consists of a substituted benzene ring, hence is classed as aromatic, with two adjacent, or "ortho-" functional groups, a carboxylic acid and an amine. The compound is consequently amphoteric. In appearance, anthranilic acid is a white solid when pure, although commercial samples may appear yellow. It is sometimes referred to as vitamin L_1 and has a sweetish taste. The anion $[C_6H_4(NH_2)(CO_2)]^-$, obtained by the deprotonation of anthranilic acid, is called anthranilate.(Mohrig, J, 1992)

Among the ligands, anthranilic acid (C6 H4 (NH2)COOH) is one of the best compound used by degrading ancient dye indigo. It is a white solid amino acid in pure form whereas commercially available in yellow form. Its molecule consists of a benzene ring with two adjacent functional groups, a carboxylic acid and an amine.(Loudon,1995)

MECHANISM



Procedure

A mass of 15 grams NAOH was desolved in 60ml water in 350 ml conical flask and cool to 0 in an ace salt bath. A mass of 13,1 grams (4.2 ml) of bromine was added in portions and then shaked well until all bromine reacted. The solution was then cooled again. A solution of 11 grams NAOH in 40 ml water was prepared. A mass of 12 grams phthalimide was added in on potion to sodium hypobromite. A stirring rod was use to stir while NAOH was being added. The mixture was warmed to 80 C for 2 minutes. A ice bath was used to cool the mixture. A volume of 30 ml concentrated hcl was added slowly until the solution was neutral. a volume of 20 ml glacial acetic acid was added to precipited the antranilic acid. A pump was used to filter the crystals. A volume of hot water was used to recrystalise with addition of a little decolouring agent. A Buchner funnel was used to collect the crystal and then dried at 100 c.

Results

TABLE: WEIGH OF ANTHRANILIC ACID

Mass of watch glass/g	43.20g
Mass of watch glass + sample/g	50.20
Mass of sample /g	7.0

CALCULATIONS

% yield = (mass of sample/theoretical mass)* 100

=(7.0 /7.0)*100

= 100 %

m.p 130

Discussion

The experiment didn't proceed very well because of a number of reasons. The bromine didn't react well the solution. This cause the solution to be brown in colour. The crystal produced were brown in colour because of bromine. This cause a very big problem when trying to recrystallize in hot water . the crystals didn't dissolve. The final yield was to high @ 7 grams indicating the presents of the impurities which is 100% yield which is impossible to attain. The melting point was to low @ 130 c which indicate some impurities as compare to the mp of the pure substance which is 145 digress. The fundamental errors also acquires which are parallax error which cause the measurement of mass and volumes to be not précises.

Conclusion

Mass of anthranilic acid	7 grams
Theoretical mass	7 grams
Melting point	130 dc
Theoretical melting point	145
% yeid	100 %

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BENZILIC REARANGEMENTS

NAME

REG NUMBER

PROGRAMME

PRACTICAL DATE

PRACTICAL NUMBER

TITLE : BENZILIC REARRANGEMENT

AIMS AND OBJECTIVES : To synthesise benzil from the oxidation of benzoin.

: To carry out a rearrangement reaction of Benzil to Benzilic acid.

: To determine the yield, M.P and I.R Spectrum of the product.

THEORY

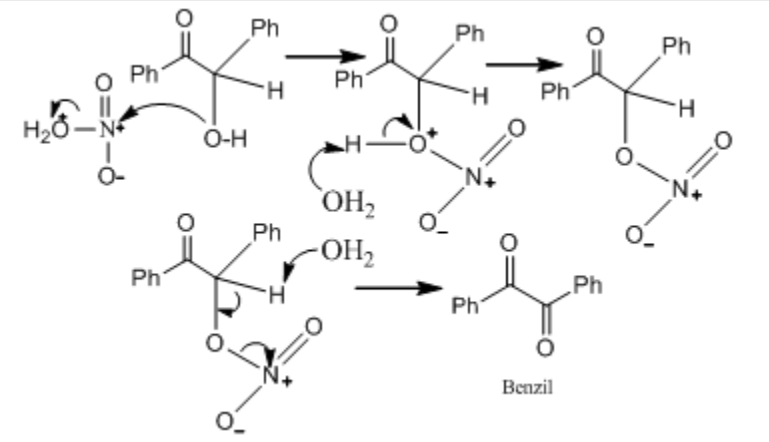
Benzilic acid is a white crystalline aromatic acid soluble in many primary alcohols.Benzilic acid rearrangements is an organic rearrangement in which benzil 1, 2-diphenyl; 1.2-dione is treated with hydroxide and then acid to give benzilic acid. The use of potassium hydroxide in benzilic rearrangement is that it acts as nucleophile and reacts with banzil, OH give electrons to benzil and break the double bond and the use of HCl in the benzilic acid rearrangement is to protonate the conjugated base of the carboxylic acid. It can be prepared by heating mixture of benzil, alcohol and potassium hydroxide. (Morrison, 1986)

The other preparation way is through benzaldehyde, which dimerizates to benzil and it is further transformed by benzilic acid rearrangement to benzilic acid. Benzilic acid is used in organic synthesis, as a base point for preparation of glycollate pharmaceuticals and some hallucinogenic drugs. Benzene acid will also be prepared by causing a rearrangement of the alpha diketone benzil. The reaction product is an α-hydroxy-carboxylic acid These rearrangements usually have migrating carbocations but this reaction is unusual because it involves a migrating carbanion.The driving force for the reaction is provided by the formation of a stable carboxylate salt .After the salt is produced ,acidification yields benzilic acid.(Mohrig, 1992)

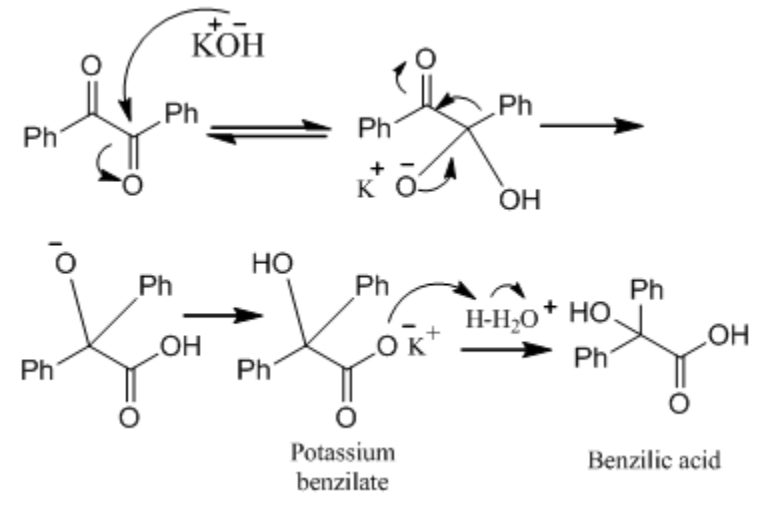
From a molecular orbital point of view this rearrangement may at a first glance not obvious. Contrary to a carbocationic rearrangement as in the Wagner-Meerwein rearrangement in which the empty carbocationic orbital interacts positively and symmetry allowed with the filled pi orbital HOMO of the central C-C bond a filled carbanionic orbital should not be able to escape a symmetry forbidden MO overlap with the LUMO which is the empty antibonding pi orbital having one node. In reality a 1,2-diketone LUMO is a 4 electron system without any nodes in the central C-C bond and a symmetry allowed transition is possible In other words the transition states of both a carbocationic rearrangement and the benzilic rearrangement obey the Woodward–Hoffmann rules because the involves respectively 2 electrons and 6 electrons (n=0 and 1 in the 4n+2 Hückel's rule). The rearrangement of benzil is base (and not acid) catalyzed under conventional conditions (water–dioxane mixture around 100 °C). (McMurry, 1984)

The rearrangement proceeds in neutral HTW without addition of base, but the yield of rearrangement products is nearly insensitive to pH at near-neutral conditions. Adding larger amounts of base, however, leads to much higher yields and 100% selectivity to rearrangement products. Likewise, adding larger amounts of acid leads to comparable yields, but less than 100% selectivity. The selectivity to rearrangement products generally increased with pH at near-neutral and basic conditions whereas the selectivity to benzil decomposition products (a competing thermal pathway) exhibited a maximum at near-neutral conditions. (Kemp, 1967)

MECHANISM



Synthesis of benzil



Synthesis of benzilic acid

PROCEDURE

A .Synthesis of benzil from oxidation of benzoin

A mass of 3.8g of benzoin was placed into a 50ml round bottom flask with 12ml of concentrated nitric acid .The mixture was heated in a fumewood on a steam bath with occasional shaking for 1hour 30mins until the brown fumes stopped. the solution was then stirred mixture of crushed ice and water ,filtered off the crystalline precipitate with suction and washed thoroughly with water.The solid was then recrystallized from 7ml of boiling ethanol.

b. Rearrangement of Benzil to Benzilic acid

A mass of 2.5g KOH was placed in 5ml of water in a 50ml round –bottomed flask and 7.5ml ethanol added with swirling.2, 5g of benzyl was then added and boiled under reflux on a water bath for 15mins.The contents were then poured into a conical flask and cooled in ice with swirling .The benzillate was filtered off at the pump and washed with 7ml ice –cold ethanol. The salt was dissolved in 25ml of water, and 2dropps of HCL added with stirring and precipitate filtered off. Gradual acidification was done with 4ml HCL until the liquid was acidic. The benzillic precipitate was filtered, washed with water and recrystallized from boiling water in activated.

TABLE 1: Synthesis of Benzil from oxidation of Benzoin.

Mass of watch glass/g	42.1g
Mass of watch glass + sample/g	45.2g
Mass of sample/g	3.1g

TABLE 2: Rearrangement of Benzilic acid

Mass of watch glass/g	42.7g
Mass of watch glass + sample/g	45.2g
Mass of sample/g	2.5g

Melting point of benzil = 97℃

Melting point of benzilic acid = 150℃

Calculations

Number of moles of benzoin used = 3.1/212.24g

= **0.014606moles**

Number of moles of benzil produced = 2.9/210.228g

= **0.01389moles**

Percentage yield of benzil = 0.01389/0.014606 ×100

= **95.09%**

Number of moles of benzil used = 2.5/210.228g

= **0.012moles**

Number of moles of benzilic acid produced = 1.7/228.24

= **0.007moles**

Percentage yield = 0.007/0.012 ×100

= **58.3%**

DISSICUSION

The experimental yield of Benzilic acid was 18.5% which was is less than the theoretical value by 81,5.On the factor of reagent transeferin the reduction of yield is reagent transfer from one container to another. Whenever substances are transferred from one container to another some of the substance remain stuck at the walls of the containers and other apparatus that come into contact with these substances.

Another factor which could have caused the reduction of yield is the purification of the product. Whenever substances are filtered small amounts of solids remain stuck on the filter paper, the more filtration steps carried out the greater the loss. Another loss was due to losses encountered during crystallisation from glacial acetic acid. During these stages not the entire product is precipitated but instead some of the product remains in the solvent. Washing of the product also results in small amounts of product being dissolved in the solvent.

Conclusion

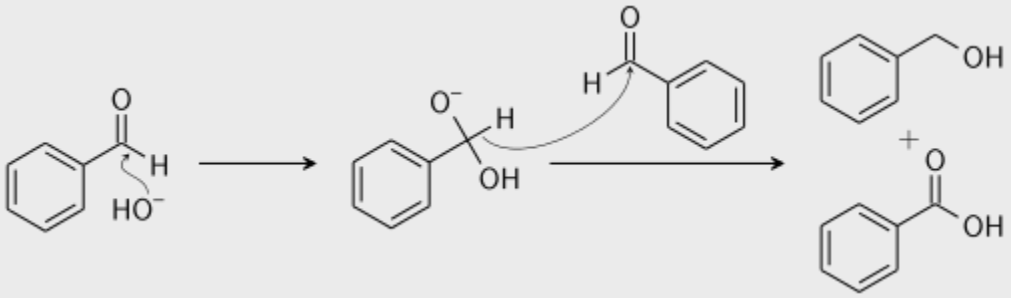
Melting point of benzil = 97℃

Melting point of benzilic acid = 150℃

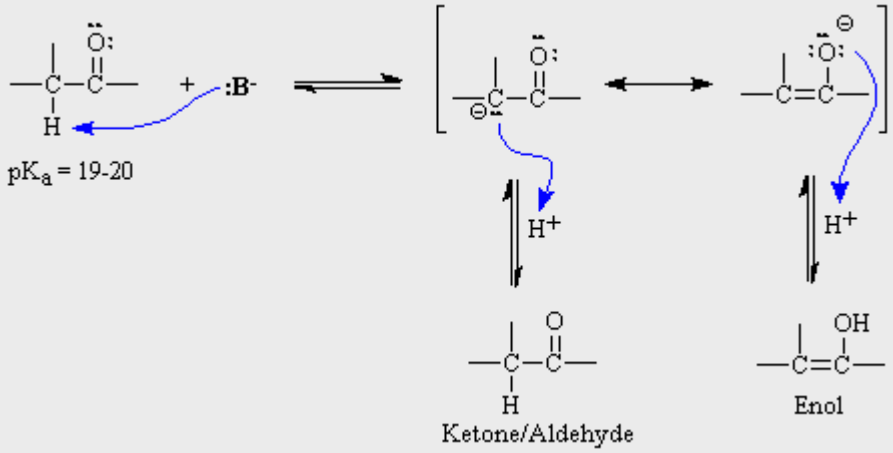
Percentage yield 95.09 %

ANSWERS TO QUESTIONS

1.



2. Alkyl hydrogen atoms bonded to a carbon atom in an (alpha) position relative to a carbonyl group display unusual acidity. While the pK_a values for alkyl C-H bonds is typically on the order of 40-50, pK_a values for these alpha hydrogens is more on the order of 19-20. This can most easily be explained by resonance stabilization of the product carbanion, as illustrated in the diagram below.



In the presence of a proton source, the product can either revert back into the starting ketone or aldehyde or can form a new product, the enol. The equilibrium reaction between the ketone or aldehyde and the enol form is commonly referred to as "keto-enol tautomerism". The ketone or aldehyde is generally strongly favored in this reaction. Because carbonyl groups are sp^2 hybridized the carbon and oxygen both have unhybridized p orbitals which can overlap to form the C=O $\pi\pi$ bond.

3. they all involve the migration of a radical from one carbon to an adjacent carbon

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ENDOLE SYNTHESIS

NAME

REG NUMBER

PROGRAMME

PRACTICAL PARTNER

PRACTICAL DATE

PRACTICAL NUMBER

TITLE **Fischer Indole Synthesis**

AIMS AND OBJECTIVES Formation of indole

THEORY

Indole is an aromatic heterocyclic organic compound. It has a bicyclic structure, consisting of a six-membered benzene ring fused to a five-membered nitrogen-containing pyrrole ring. Indole is widely distributed in the natural environment and can be produced by a variety of bacteria Indole is a solid at room temperature. Indole can be produced by bacteria as a degradation product of the amino acid tryptophan. It occurs naturally in human feces and has an intense fecal odor. At very low concentrations, however, it has a flowery smell,[3] and is a constituent of many flower scents (such as orange blossoms) and perfumes. It also occurs in coal tar. (Kemp,1967)

The Fischer indole is a chemical reaction that produces the aromatic heterocycle indole from a substituted phenyl hydrazine and an aldehyde or ketone under acidic conditions. The mechanism begins with formation of a phenylhydrazone through the acid catalyzed reaction of the hydrazine with the carbonyl. The phenylhydrazone then rearranges to the enamine and gets protonated on the phenyl nitrogen. An "ene reaction" (3,3-sigmatropic rearrangement) ensues, resulting in a diimine and loss of aromaticity. Additional key steps include rearomatization, formation of a cyclic aminal, and the expulsion of ammonia to give the indole product. Antimigraine drugs of the triptan class are often synthesised by indole .the choice of the acid catalyst is very important .Bronsted acids such as HCl H_2SO_4 phosphoric acid and p toluenesulfonic acid have been successfully. . Lewis acids such as boron trifluoride, zinc chloride, iron chloride, and aluminium chloride are also useful catalysts. (McMurry, 1984)

Via a palladium-catalyzed reaction, the Fischer indole synthesis can be effected by cross coupling aryl bromides and hydrazones. This result supports the previously proposed intermediacy as hydrazone intermediates in the classical Fischer indole synthesis. Using palladium chemistry developed at MIT by Stephen Buchwald, the Fischer indole synthesis can be completed using aryl bromides as starting materials. These N-aryl hydrazones undergo exchange with other ketones, expanding the scope of this method. Fischer indole synthesis is a well established procedure for the synthesis of substituted indoles. Several members of the indole alkaloid familiy, flavopereirin and sempervirin among them, have shown antitumor activity.Since our drug-development efforts focus on the indoloquinolizinium moiety, recently we have become interested in synthesizing substituted tryptamines as intermediates for the synthesis of indoloquinolizinium analogues with enhanced antitumor activity. In order to guide the synthetic process, we started a theoretical study of the mechanism of the Fischer indole synthesis, so we could gain a better understanding of the electronic factors that influence the course of the reaction.(Mohrig, 1992)

It has been reported[2] that such a large amount of zinc chloride is not necessary, but the submitters found that equal parts of acetophenone phenylhydrazone and zinc chloride gave lower yields. Using 3.2 times the quantities specified above, except that no sand was added in separating the product, the checkers have obtained yields of 75–80% of 2-phenylindole.. While drying, the surface of the product becomes very light green. The filtrate still contains some 2-phenylindole, but great difficulty is encountered in trying to purify the crude material. Only the C-2 to C-3 pi-bond of indole is capable of cycloaddition reactions. Intermolecular variants are often higher-yielding than intermolecular

cycloadditionsThe most reactive position on indole for electrophilic aromatic substitution is C-3, which is 10^{13} times more reactive than benzene. For example, it is alkylated by phosphor.(streitwiser, 1976)

PROCEDURE

Placed acetophenone (2ml), phenylhydrazone (1.8ml) and 3 drops of glacial acetic acid in a boiling tube. Crystals of hydrazone will rapidly separate. Added 5g of powdered anhydrous zinc chloride ,heat gently and stir the mixture with a thermometer, until the ring closure-reaction begin(130-140^{o}C).As soon as the reaction occurs considerable heat is generated and the reaction mixture must be immediately cooled by immersion in beaker of cold water with stirring to prevent any local overheating. The temperature must not be allowed to exceed 180^{o}C. When the main reaction has finished, keep the temperature at 130-140^{o}C for further five minutes with stirring. Cool slightly, and glacial acetic acid (15ml), heat to dissolve the product, pour the solution into a beaker and allow to recrystallize. After the bulk of the product has recrystallized, add 20ml water. Product filtered at the pump, wash with a small quantity of 75% aqueos EtOH and recrystallize the crude solid from aq.EtOH. Dry the crystals at tube pump and finally dry in an air oven at 60^{o}C.

TABLE 1: WEIGHING OF INDOLE

Mass of watch glass/g	30.0g
Mass of watch glass + sample/g	32.0g
Mass of sample/g	2.0g

Table 2:Interpreted IR Spectrum for 2 phenylindone

FUNCTIONAL GROUP	WAVE NUMBER
C-H aromatic	3100
C-H PHENYL RING	725
C-H alkane	2800

C=C aromatic	1575
N-H	3600

MP=52-54 degree celcius

DISSICUSION

A poor percentage yield was obtained of 51,9 % this was mainly contributed by the loss of the sample during recrystalisation and also the filtering procedures in retaining the yield would have been lost , indole which is a major constituent of coal tar , and 220 -260 ^{o}C distillation fraction , shows that it a moderately high temperature hence losses may not be accounted for heating with temperatures below 200 . The colour of the indole sample that was obtained upon drying was rather whitish though the sample contained some brownish impurities that may not have had washed away properly by the recrystalisation process and filtering off the sample by high concentrations of alcohol.

CONCLUSSION

Theoretical mass of indole/g	3.8512g
Experimental mass of indole/g	2.0g
% yield of indole	51.9%

Mp=52-54 degree Celsius

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SYTHESIS OF ANTHRAQINONE

NAME:

REG N^{O}:

PROGRAM:

COURSE:

PRAC N^{O}:

DATE:

TITLE:

OBJECTIVE:

INTRODUCTION

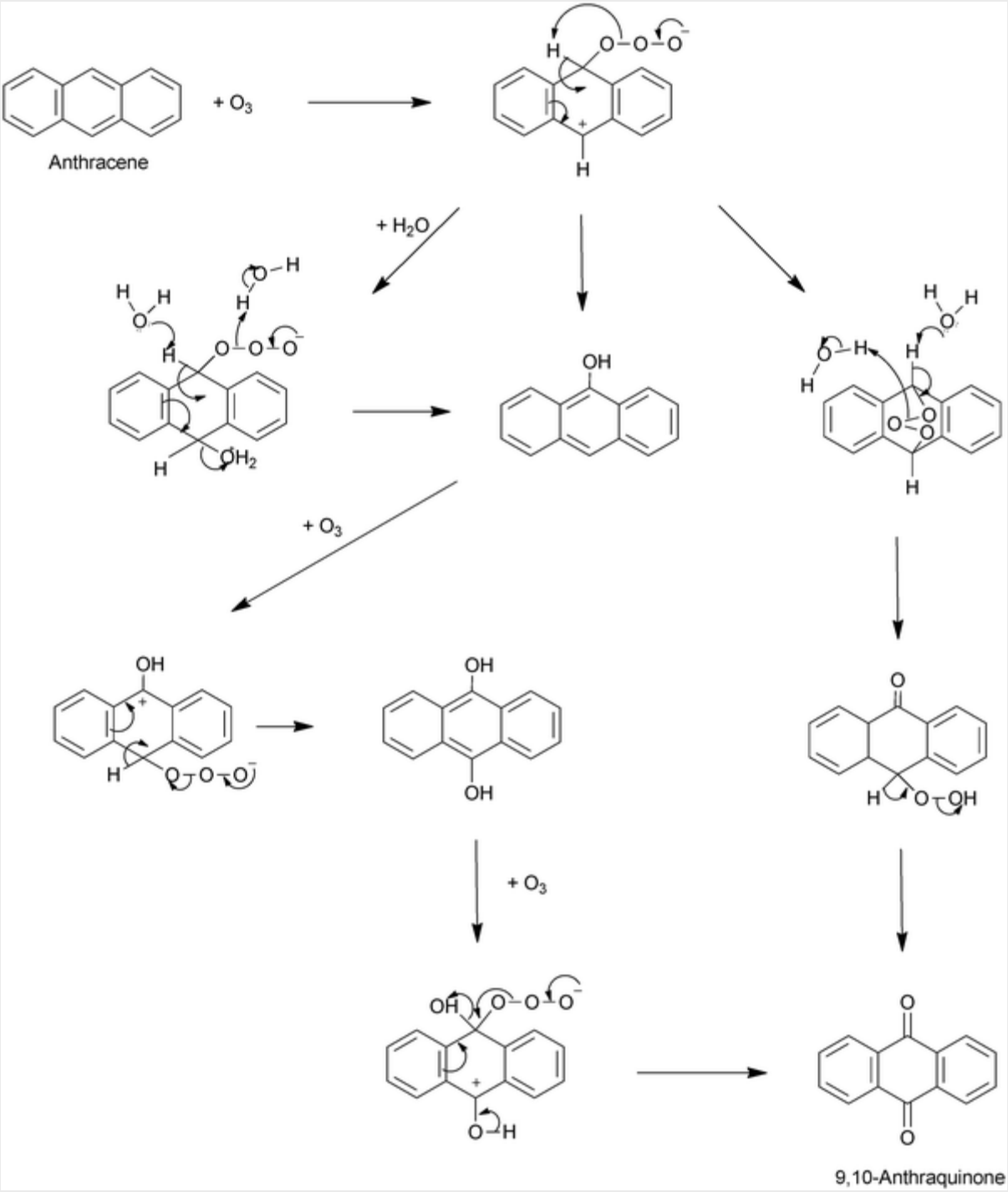
Anthraquinone is also known as anthracenedione or dioxoanthracene. It is an aromatic organic compound with the formula $C_{14}H_8O_2$. There are several possible Anthraquinone isomers. Anthraquinone refers to the 9, 10 Anthraquinone which is a yellow highly crystalline solid. Anthraquinone is poorly soluble in water but highly soluble in organic solvents. (Lednicer and Mitscher, 1977)

The oxidation of anthracene with cerium (IV) ammonium nitrate appears to occur through an initial anthracene radical cation which is transformed into a transient anthrol nitrate. Homolysis of the oxygen–nitrogen bond of the anthrol nitrate furnishes the nitrite radical and a mesomeric anthrone radical. While the former attacks the initial ion radical with a concerted mechanism to yield anthrol nitrite, the latter undergoes dimerization to bianthrone, addition of a nitrate radical to yield 9, 10-dihydro-10-oxo-9-anthryl nitrate which subsequently disproportionates to Anthraquinone and nitrous acid, and oxidation to the anthrone cation. This is attacked by a nucleophile to yield 10-methoxyanthrone or 10-acetoxyanthrone according to the solvent used. (Clayden, 2012)

Ceric ammonium nitrate in acetonitrile nitrates benzene. Naphthalene and anthracene are nitrated and also oxidized to quinones. The mechanism of nitration is not known but radical cations may be involved. Metal nitrates have often been used in solution in acetic acid. These systems are advantageous with very reactive and acid sensitive compounds. (Lednicer, 2008)

Anthraquinone is used as a digester additive in production of paper pulp by alkaline process, like the Kraft, the alkaline sulphite or soda AQ process. Anthraquinone is a redox catalyst, with the reaction mechanism involving single electron transfer. The Anthraquinone is oxidizing the reducing end of polysaccharides in pulp that is cellulose and hemillose thus protecting it from alkaline degradation. Anthraquinone is reduced to 9, 10 dihyroxyanthracene which then reacts with lignin. The lignin is degraded and becomes water soluble and washes away from the pulp while Anthraquinone is regenerated. This therefore increases the pulp yield and reduces kappa number. (Edenborough, 1999)

MECHANISM



(Monson, 1971)

PROCEDURE

A mass of 0.356g of anthracene and 13ml of tetrahydrofuran were placed in a 50ml round bottomed flask and 4ml of water was added whilst stirring. A white suspension was formed and 4.39 ammonium cerium (IV) nitrate was added to the suspension and the mixture was allowed to stir for a further 5 minutes on a magnetic stirrer. The solvent was then evaporated to about 3ml on the rotary evaporator at 70℃ of water temperature. The residue consisted of an aqueous phase and a solid. The aqueous phase was decanted during filtration of the solid. To remove any water soluble components the solid was washed thoroughly with 30ml of water before being filtered. The solid was dried at the pump and the crude product was recrystallized from 2ml glacial acetic acid and filtered at the pump. The melting point was determined.

RESULTS

Table 1: Weighing of Anthraquinone

Mass of sample+ container / g	15.5
Mass of empty container / g	15.0
Mass of sample / g	0.5

Melting point = 285℃

CALCULATIONS

Number of moles of anthracene used = 0.356/178.2

=**0.002moles**

Number of Anthraquinone produced= 0.5/208.2

= **0.002mols**

Percentage yield = actual moles/ theoretical moles × 100

= 0.002/0.002×100

= **100%**

DISCUSSION

The experiment was carried out and proceeded as expected. The theoretical and experimental yield tallied. The crystals were finely separated and bright yellow. This showed proper drying and with no water. If water was present a crude product would have been produced. The theoretical melting point and the actual melting point tallied. This shows the absence of impurities. Impurities alter the melting point and cause the product to melt over a wide temperature range.

CONCLUSION

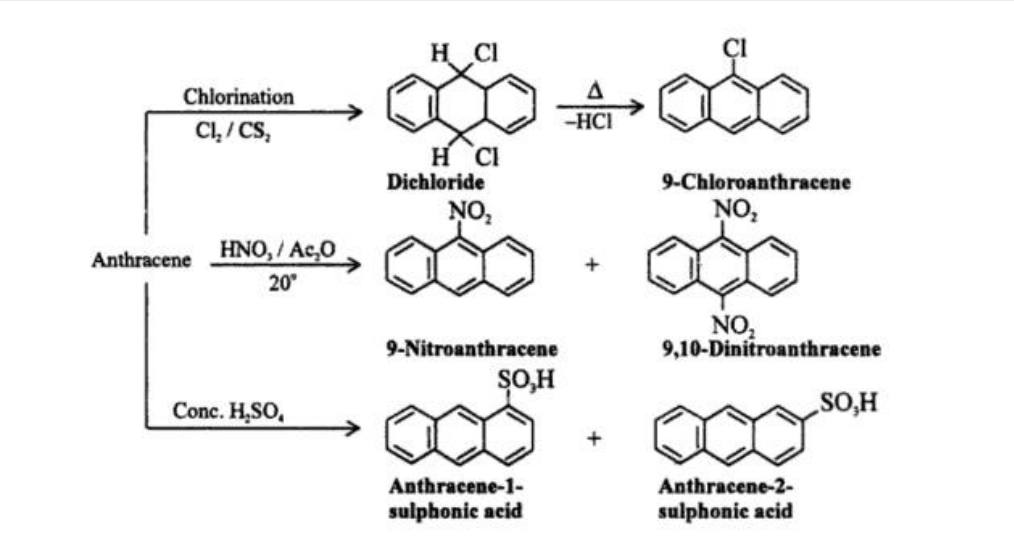
A yellow high crystalline solid was formed.

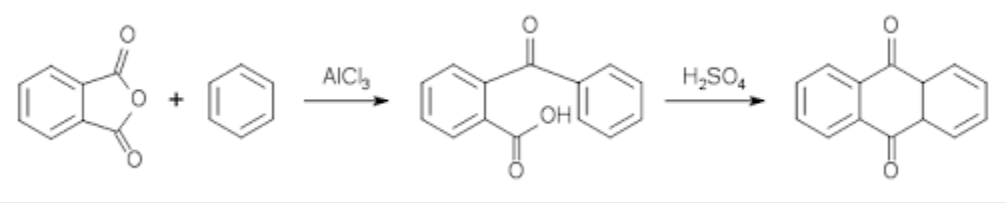
The melting point was 285℃.

The percentage yield was 100%

ANSWERS TO QUESTIONS

1.





The intermediate is benzilic acid.

2. 2-Methyl-1-nitro-9,10-anthraquinone

3.

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FLAME ATOMIC ABSOBTION SPECTROSCOPY
DETEMINATION OF HARDNESS OF WATER

Name :

Registration number :

Practical partner :

:

Date experiment was done:

Title for the experiment : **flame atomic absorption spectroscopy**

: **Determination of the hardness of water**

Objective ; Determination of the concentration of Mg and Ca in Unknown sample K

Theory

Until recently ,flame atomic absorption spectroscopy was the most widely used of all atomic spectral methods because of its simplicity, effectiveness, and relatively low cost .Water hardness is determined by the total concentration of magnesium and calcium The hardness of a water source has important economic and environmental implications. Currently, titration methods are the most common protocol for the determination of water hardness, but investigation of instrumental techniques can improve efficiency. Atomic spectroscopy is one of the most widely used methods for quantitative elemental analysis. But to do the analysis, the sample has to be completely destroyed (chemically and physically) and reduced to individual gas phase atoms in well defined states. This requires a very highly energetic environment and a lot of modification of the sample, both of which lead to a number of complications. Hard water also forms deposits that clog plumbing. These deposits, called "scale", are composed mainly of calcium carbonate ($CaCO_3$), magnesium hydroxide ($Mg(OH)_2$), and calcium sulfate ($CaSO_4$). Calcium and magnesium carbonates tend to be deposited as off-white solids on the surfaces of pipes and the surfaces of heat exchangers. This precipitation is principally caused by thermal decomposition of bi-carbonate ions but also happens to some extent even in the absence of such ions. (Ben, 1994)

The most common instrument components consist of a hollow cathode lamp source, a pneumatic nebulizer for an atomizer, a conventional grating monochromator and photomultiplier tube detector .The hollow cathode lamp is made of a glass envelope with a quartz window filled with an inert gas at slightly above atmospheric pressure .The cathode is made of the pure metal of interest .The pneumatic nebulizer aspirates and nebulizes the liquid sample solution when the sample is sucked through a capillary tube .The grating monochromator eliminates much of the background light from the flame and the photomultiplier tube detector detects that light from the hollow cathode lamp which passes through the flame. (Skoog et al, 1991)

The most common source for atomic absorption measurements is the hallow cathode lamp, which consists of a tungsten anode and a cylindrical cathode sealed in a glass tube that is filled with neon or argon at a pressure of 1 to 5 torr .The cathode is constructed of the metal whose spectrum is desired to support a layer of the metal .the efficiency of the cathode lamp depends upon its geometry and the operating potential .In the typical atomic absorption instrument it is necessary to eliminate interferences caused by emission of radiation by the flame .Much of these emitted radiation is ,of course ,removed by the monochromator .(Ewing,1994)

AA spectroscopy is highly specific, which can be a disadvantage when you're trying to analyse a mixture. Each element has to be tested separately .The samples and standards have to be in solution, or at least volatile .A large number of interferences are possible, such as the formation of non-volatile compounds, smoke formation which will absorb light, contamination. Relative precision of the method is quite low .Another principal errors encounted are variations in the flame background and contamination of the abundance of sodium in the atmospheric dust, it is necessary to filter air entering the burner housing. (Bill. 1966)

Radiation interferences caused by elements other than that being determined are the greatest contributor to error in flame photometry .However, the effects may be minimised by operating at the lowest practical Na or K concentration range or by removal of the interfering elements. For example Al has a depressing effect on alkali metal emission, which may be of serious consequence. (Fries, 2008)

APPARATUS

Flame atomic absorption spectrometer

Volumetric flasks, 2* 1000ml; 8*100ml

Procedure

A Stock solutions of 1000 ppm Ca^{2+} and Mg^{2+} were prepared separately in 100 ml volumetric flask and filling to the mark with deionised water. A working solution of 100ppm magnesium was prepared from the stock solution in to the 100 ml volumetric flask. Five calibration solutions of concentrations 1,3,6,9,12ppm for Ca^{2+} and 0.1;0.2; 0.4; 0.6; 0.8ppm for Mg^{2+} were prepared followed by the addition of 2ml of 10% (w/v) solution of strontium into each flask before adding to the mark with deionised water. Composite calibration standards were prepared having both Mg and Ca in on flask i.e. 1 ppm Ca^{2+} and 0.1 ppm Mg^{2+} were prepared in the same volumetric flask. Sample k was given for determination of water hardness. The instrument settings were optimised. The absorption of the calibration solutions were measured and a plot of absorption as a function of concentration was constructed. The sample k was run and the concentrations of Ca^{2+} and Mg^{2+} in the sample K was detemined .

DATA

Table 1:Weighing of magnesium ribbon in g

mass of magnesium ribbon and watch glass\g	16.689
mass of watch glass only \g	16.589
Mass of magnesium ribbon\g	0.1000

Table 2; Weighing of $Caco_3$ in grams

Mass of sample and watch glass \g	17.4797
Mass of watch glass only \g	17.2300
Mass of sample \g	0.2497

Preparation of the calibration solutions:

Concentration of working standard = 100ppm

Volume to be made = 100ml

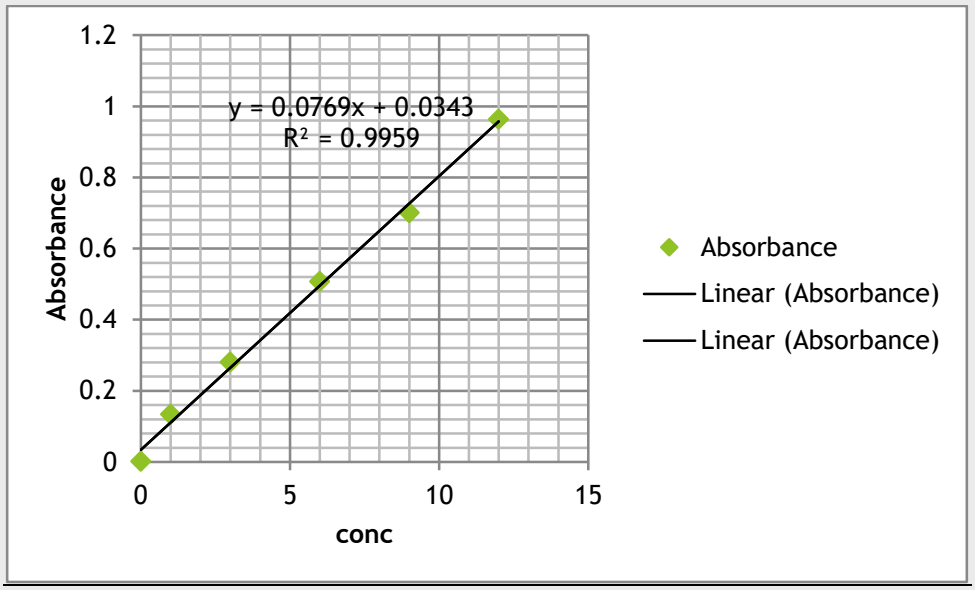
Formula: $C_1V_1 = C_2V_2$

	Conc. of calibration std/ppm (Ca)	Volume to be diluted up to 100ml	Conc. of calibration std/ppm (Mg)	Volume to be diluted up to 100ml
Std 1	1.0	0.1	0.1	0.1
Std2	3.0	0.3	0.2	0.2
Std3	6.0	0.6	0.4	0.4
Std4	9.0	0.9	0.6	0.6
Std5	12	1.2	0.8	0.8

RESULTS

Calibration curve of calibration standards: [Ca^{2+}]

Solutions	Conc./ppm	Absorbance
Blank	0.0000	0.0016
Std1	1	0.1340
Std2	3	0.2811
Std3	6	0.5075
Std4	9	0.7011
Std5	12	0.9641



Calibration table of [Ca] in sample :k

	Concentration/ppm	Absorbance
First run	6.0046	0.5030
Second run	6.0181	0.5040
average	6.0113	0.5035

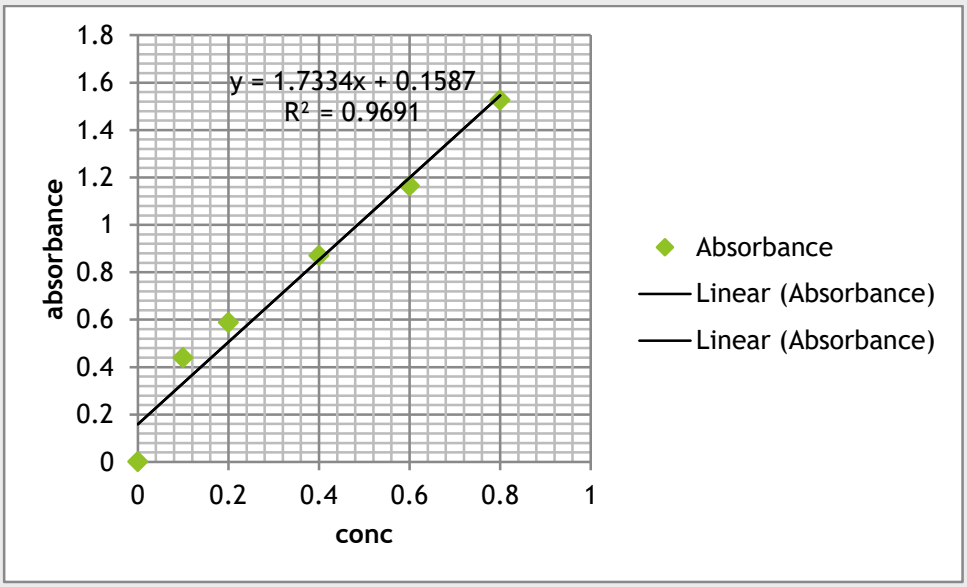
SD = 0.0007

CV= 0.1414%

Calibration table for [Mg] in calibration solutions

Solutions	Concentration/ppm	Absorbance
Blank	0.0	0.0007
Std1	0.1	0.4403
Std2	0.2	0.5889
Std3	0.4	0.8705
Std4	0.6	1.1651
Std5	0.8	1.5272

Calibration curve of Mg^{2+}



Calibration of $[Mg^{2+}]$ in sample K

	Concentration/ppm	Absorbance
First run	0.4280	0.9307
Second run	0,4283	0.9311
avarage	0.4282	O.9309

SD =O.003

CV=0,0325%

Calculations

Calculating $[Ca^{2+}]$ in sample k:

absorbance of k= 0,5035

Substituting k in: y=0.0769x + 0.0343; were x= [Ca]

0.5035=0.0769x + 0.0343

X=6.101430 ppm

Calculating [Mg] in sample J

absorbance= 0.9309

Substituting k absorbance in: y=1.7334x + 0.1587

0.9309 =1.7334x + 0.1587

X= 0.4455 ppm

X = [Mg]

Water hardness of sample k:

$[Ca^{2+}]$ = 6.1014 ppm $[Mg^{2+}]$ = 0.4455 ppm

Sum of the concentrations = 6.5469 ppm

Since 10mgCaO/l H_2O = 1°dH, therefore 6.5469 mg CaO/l H_2O

= 0.6469°dH

Discussion

The experiment proceeds as expected. The solutions were prepared accurately with great precision. Despite the care taken when preparing these solution some error acquired as shown in the calibration curves. These errors might have risen from parallax, chemicals which are not up to analytical grade, radiation interference caused by elements other than that being determined, For example Al has a depressing effect on alkali metal emission which may be of serious consequences , variations in flame background and contamination and other unknown factors. Parallax error is error that arise from incorrect reading of the liquid meniscus. This error cause the volume to be more or less which greatly affect the concentration of Mg Ca in the solution. This account for the slight deviation from straight line of the calibration curve. This error might have reduced by extremely accurately reading exactly below the meniscus. The chemicals used in preparation of solutions were not of analytical grade. This means they carry impurities which interferes with our results. This source of error might have reduced my using analytically pure chemicals. The hardness of sample k is 6.5469 ppm which is less than 60 ppm this means that sample k is considered soft. The accuracy of the flame spectrometer made it the right choice for the determination.

CONCLUSION

Regression equation Mg calibration $y=1.7334x + 0.1587$

R^2 Value = 0.9691
[Mg] = 0.4455 ppm

Regression equation Ca calibration $y=0.0769x + 0.0343$
R^2 Value = 0.9979

[Ca] = 6.101430 ppm

Hardness of sample k = 6.54693 ppm
= 0.6469°dH

Reference

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FLAME ATOMIC EMISSION SPECTROSCOPY
DETERMINATION OF SODIUM IN DRINKING WATER

NAME

REG NUMBER

PROGRAMME

PRACTICAL PARTNER

PRACTICAL DATE

PRACTICAL NUMBER

TITLE	FLAME ATOMIC EMISSION SPECTROSCOPY :Determination of sodium in drinking water.
AIMS AND OBJECTIVES	-To determine the sodium concentration in drinking water using the flame atomic emission spectroscopy.

THEORY

Flame photometry, now more properly called flame atomic emission spectrometry or "flame photometry" is a relatively old instrumental analysis method. Its origins date back to Bunsen's flame-color tests for the qualitative identification of select metallic elements. As an analytical method, atomic emission is a fast, simple, and sensitive method for the determination of trace metal ions in solution. Because of the very narrow (ca. 0.01 nm) and characteristic emission lines from the gas-phase atoms in the flame plasma, the method is relatively free of interferences from other elements. Typical precision and accuracy for analysisof dilute aqueous solutions with no major interferences present are about ±1-5% relative. Detection limits can be quite low. "Good" elements typically have detection limits between about 1 ng/mL and 1 µg/mL. The method is suitable for many metallic elements, especially for those metals that are easily excited to higher energy levels at the relatively cool temperatures of some flames – Li, Na, K, Rb, Cs, Ca, Cu, Sr, and Ba. Metalloids and nonmetals generally do not produce isolated neutral atoms in a flame, but mostly as polyatomic radicals and ions. Therefore, nonmetallic elements are not suitable for determination by flame emission spectroscopy, except for a very few and under very specialized conditions. (8)

Flame photometry is a type of atomic EMISSION spectroscopy. The sample is excited (raised to a high temperature), causing the emission of light. the wavelength of the emitted light is a function of the energy of the excited electrons, so each element has a characteristic set of wavelengths, usually a single wavelength is detected and the intensity of the emission is used to calculate concentration.Flame atomizers are used for atomic emission measurements, it consist of a nebulizer, which converts the sample solution into a mist or aerosol that is then fed into a burner. The liquid sample is sucked through a capillary tube by a high pressure stream of gas flowing around the tip of the tube. This process of liquid transport is called aspiration. The high velocity gas breaks the liquid up into fine droplets of fine droplets of various sizes which are then carried into the flame. Atomization takes more quickly when organic solvents are used than water.9

A sample of the material is brought into the flame by aspiration. The heat from the flame evaporates the solvents and break chemical bonds to create free atoms. The thermal energy excites the atoms into exited electronic states that subsequently emit light when they return back to the ground electronic state. Each element emits light at a characteristic wavelength, which is dispersed by a grating or prism and is detected in the spectrometer. (Berg, 1983)

Spectral emission lines are generated by the exited atoms formed during the process of combustion in the flame. The intensities and wavelengths of emission lines are measured in flame photometry. The intensity of emission depends on the concentration of an element in the sample, the rate at which the exited atoms are formed. The latter depends on the rate at which the sample is introduced in the flame, the temperature of the flame and the composition of the flame. The flame temperature is controlled by the type of fuel and oxidant used .Common oxidants used are air, oxygen and nitrous oxide and the fuels are hydrogen, acetylene and propane. An oxidation-reduction takes place, with the oxidant oxidising the fuel. An increase in the flame temperature causes an increase in emission intensity. (Robinson, 1987)

The presents of a certain element can be detected visually as in the case of a yellow flame produced by sodium. The yellow radiation from sodium impurities in the sample is often tense enough to mask radiation from other elements present. Calibration curves are prepared by making up standard solution of known concentration similar to those expected in the sample. The curve relating the emission intensity and the concentration of sodium is the calibration curve. The relationship between the emission intensity and concentration is linear at low concentrations but deviates from linearity at high concentrations. There is a relative decrease in intensity as concentration increases. (Heineman, 1989)

APPARATUS

-volumetric flask *12

-pipette

-wash bottle

-beaker

-spatula and wash glass

PROCEDURE

0,25435g of NaCl salt was weighed and 1000ppm stock solution of Na+ was made by dissolving the NaCl salt in de-ionised water. Calibration solutions of concentrations 1.0, 2.0, 4.0, 8.0, 10.0 and 12.0ppm Na+ was prepared using the stock solution by diluting with de-ionised water which was filled to the mark of a 100ml volumetric flask. Sample H and K was diluted using de-ionised water and were filled to the mark. The wavelength of the spectrophotometer was set to 589.0nm.The calibration solution of 12.0ppm Na+ was run, adjusting the emission to 100% and its emission was measured. This was repeated again for calibration solutions of 10.0, 8.0, 4.0, 2.0 and 1.0ppm respectively. Sample solutions G, H and K were run and their emission was measured.

RESULTS

Table 1: Mass of NaCl

Mass of container + sample	
Mass of container	
Mass of sample	

Table 2: Emissions of the Na^+ calibration solutions at 580 nm

SOLUTION	CONCENTRATION (ppm)	EMISSION INTENSITY
Std 1	1.0000	0.1860
Std2	2.0000	0.2415
Std 3	4.0000	0.3274
Std 4	8.0000	0.4429
Std 5	10.0000	0.4889
Std 6	12.0000	0.5344

Table 3: Determination of $[Na^+]$ in sample J

	Concentration (ppm)	Emission intensity
1st run	7.7604	0.4196
2nd run	7.7771	0.4202
3rd run	7.8273	0.4217
Average	7.7883	0.4205
Standard deviation	0.0011	0.0011

Table 4: Determination of $[Na^+]$ in sample T

	Concentration (ppm)	Emission intensity
1st run	5.9225	0.3626
2nd run	5.9235	0.3627
3rd run	5.9309	0.3629
Average	5.9256	0.3627

Standard deviation	0.0001	0.0001

Table 5: Determination of [Na^+] in sample U

	Concentration (ppm)	Emission intensity
1st run	4.1417	0.3074
2nd run	4.1259	0.3069
3rd run	4.1570	0.3079
Average	4.1415	0.3074
Standard deviation	0.0005	0.0005

CALCULATIONS

y =0.0372x +0.0881

[Na+] in sample G

0.2356 = 0.0372x +0.0881

x =0.2356- 0.0881/0.0372

x =3.9651ppm

therefore [Na+]= 3.9651ppm

[Na+] in sample in H

0.2550 = 0.0372 + 0.0881

x = 0.2550 – 0.0881/0.0375

x =4.487 *5 dilutions

Therefore [Na+] =22.435 ppm

[Na+] in sample in K

0.2851 = 0.0372x + 0.0881

x = 0.2851-0.0881/0.0372

x =5.295 *5 dilutions

Therefore [Na+] = 26.479ppm

Discussion

In this experiment ,the calibration curve for flame emission obtained was a linear over 3 order of magnitude with ionisation limiting linearity when the analyses' concentrations is small and self absorbance limiting linearity for higher concentration of analyse. Therefore there is a relative decrease in intensity as the concentration increases. Emission intensity may have been affected significantly by the temperature of the excitation source and efficiency of atomisation. Error could have been resulted from inaccurate preparation of solutions with known sodium concentrations causing the calibration curve to be inaccurate. Errors could have been minimised by calibrating the photometer in between each trial using the blank.

Conclusion

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UV VIS SPECTROSCOPY
COULORIMETRIC DETERMINATION OF PHOSPHORUS IN COLA DRINKS

NAME

REG NUMBER

PROG

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TITTLE **UV- VIS SPECTROSCOPY**

AIM - Coulorimetric determination of Phosphorus in Cola Drinks

THEORY

UV-visible spectrophotometry is an important method of quantitative analysis with applications in environmental, clinical, industrial and forensics. The reasons for its popularity are because it allows measurement of trace elements of up to 10-5 molar and impurities to be determined directly with high sensitivity and accuracy. It also has a wide application in both organic and inorganic systems and is easy to retrieve data. The method is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied (Skoog, et al., 2007)

A spectrophotometer can be either single beam or double beam. In a single beam instrument, all of the light passes through the sample cell. It must be measured by removing the sample. In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. The reference beam intensity is taken as 100% Transmission or 0 Absorbance, and the measurement displayed is the ratio of the two beam intensities.(Christian G.D and O'Reilly J.E, 1986)

Soft drinks are complex mixtures containing variety of substances such as colouring compounds, flavouring agents, acidifiers, sweeteners, preservatives and caffeine. The most common acidifier used in soft drinks is phosphoric which gives a tangy taste in the mouth. Phosphoric acid can also acts as a preservative, keeping the contents of the bottle fresh.Colometric analysis for determining the amount of an inorganic compound in solution involves a reaction between an organic reagent and an analyte to form a colored complex. The reaction can be used to determine analyte concentrations assuming the colour intensity and absorbance is proportional to the analyte concentration.

Phosphate ion reacts with molybedic acid to form phosphomolybdate, a complex ion. The phosphomolybdate,a on reduction forms another complex, called molybdenum blue which can be monitored colourimetrically.A colorimeter can be used to measure any test substance that is itself coloured or can be reacted to produce a colour. (Willard, et al, 1974)

Molecules containing pi electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals.In. The more easily excited the electrons (that is lower energy gap between the HOMO and the LUMO),the longer the wavelength of light it can absorb.UV/VIS spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes,such as transition metal ions, highly conjugated organic compounds and biological macromolecules. Spectroscopic analysis is commonly carried in solutions but solids can also be studied. (Dean, 1995)

The Beer Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in solution and the path length.Thus, for a fixed path length, UV/VIS spectroscopy can be used to determine the concentration of the absorber in a solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a calibration curve. The Beer Lambert law states that: $A=\log_{10}(I_0/I) = \varepsilon cL$, where A is the absorbance,I_0 is the

intensity of the incident light at a given wavelength,*I* is the transmitted intensity is the pathlength through the sample, and c is the concentration of the absorbing species. (Scheck. and Fritz, 1975)

The Beer –Lambert law has implicit assumptions that must be met experimentally for it to apply otherwise there is a possibility of deviations from the law to be observed. For example the chemical makeup and physical environment of the sample can alter its extinction coefficient. The chemical and physical conditions of a test sample therefore must match reference measurements for conclusions to be valid. (Smith, 1981)

MATERIALS

- UV –VIS Spectrometer (SHIMADZU)
- Water bath

RESULTS

Table 1: Weighings of potassium dihydrogen phosphate

Mass of watch glass + sample/g	17,7564
Mass of watch glass/g	17,6129
Mass of sample/g	0,1435

Table 2: Weighings of ammonium heptamolybdate/g

Mass of sample + watch glass/g	18.6132
Mass of watch glass/g	17,6129
Mass of sample/g	1.0003

Table 3: Weighings of ascorbic acid/g

Mass of sample + watch glass/g	19.3634
Mass of watch glass/g	17,6129
Mass of sample/g	1.7505

Table 4: Absorbances of calibration solutions

Standard number	Concentration	Absorbances
1	0	0.002
2	0.4	0.104
3	0.8	0.204
4	1.6	0.427
5	2.4	0.644
6	3.2	0.863

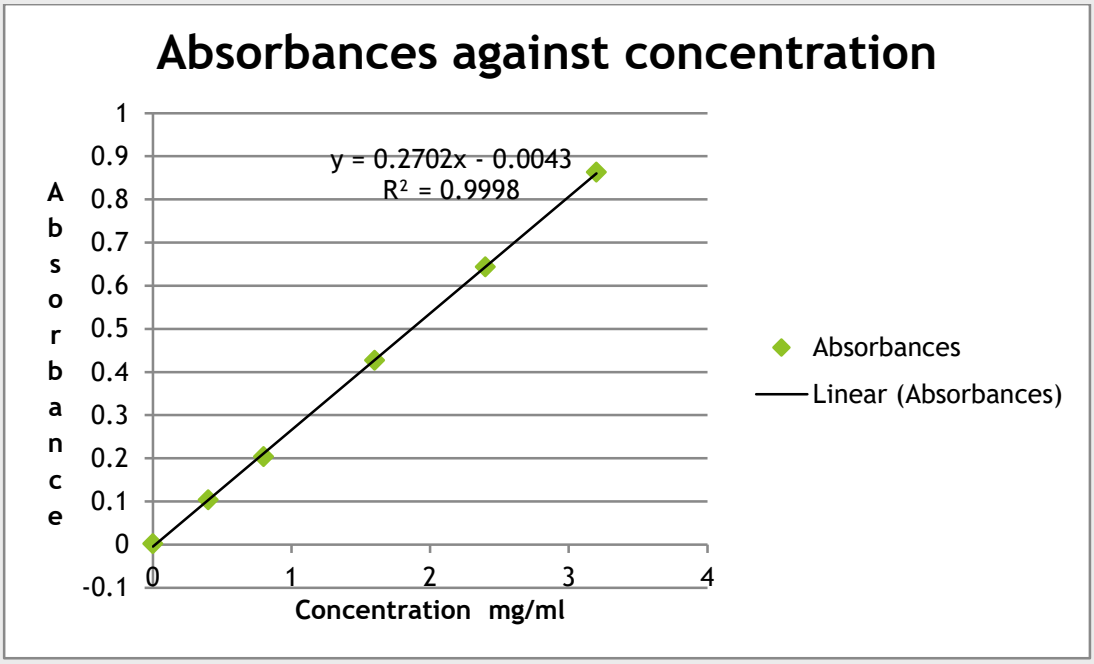

Table 5: Absorbances for the sample

Sample	Concentration	Absorbance
1	1.0812	0.288
2	1.0886	0.290
3	1.1042	0.294

CALCULATIONS

Stock Solution

Mr of [KH_2PO_4] =136.10

Mr of [PO_4^{3-}] =94.97

Mr (KH_2PO_4)/Mr (PO_4^{3-})

$=\frac{136,1}{94,97}$

=1, 43g

1000ppm: 1.43g [KH_2PO_4] in 1000ml deionized water

In 100ml:$\frac{100}{100}$ × 1,435g

=0,143g

Therefore 0, 143g of KH_2PO_4 was dissolved in 100ml deionized water

Working Standard solution

$C_1V_1=C_2V_2$

$1000(V_1) =10(100)$

V_1 = 1ml

Therefore 1ml of the stock solution was pipeted into a 100ml volumetric flask and filled up to the mark with deionized water.

Sample

20×dilution in a 50ml volumetric flask

50/20=2,5ml

2,5ml of cola drink was diluted up to the mark in a 50 ml volumetric flask

Calibration solutions (Standards)

$C_1V_1=C_2V_2$

10(V1) =0, 4(50)

For 0,4ppm V_1=2ml

For 0.8ppm V_1 =4ml,

For 1.6ppm V_1 =8ml,

For 2.4ppm V_1 =12ml,

For 3.2ppm V_1=16ml

Concentration of phosphorus in the sample

Concentration of phosphorus in the sample was (1.0812+1.0886+1.1042)/3

= 1.0913mg/ml

Average absorbance = (0.288+0.290+0.294)/3

= 0.872/3

= 0.291

To calculate the concentration of the P in cola sample

From Graph 1: $y = 0.270x - 0.004$

When y=0.291

Then: $0.291 = 0.270x - 0.004$

$0.270x = 0.291+0.004$

0270x=0.295

$\therefore \quad x = 1.093$ mg/ml

X dilution factor of 500

= 546.296ppm

- Standard Deviation At 95% Confidence Level: $s = \frac{\sqrt{\sum(x-\bar{x})^2}}{\sqrt{(n-1)}}$

$$= \sqrt{\frac{(0.288-0.291)^2+(0.290-0.291)^2+(0.296-0.291)^2}{(3-1)}}$$

$$= \sqrt{\frac{0.000035}{(2)}}$$

= 0.0041833

95% Confidence limits of the cola sample $= \bar{x} \pm \frac{ts}{\sqrt{n}}$

$\bar{x} = 0.291$

t =4.30 (from t tables)

s=0.0041833 (standard deviatiuon)

n=3

E= $0.291 \pm (4.30\ x\ 0.0041833)\ /\sqrt{3}$

= $0.291 \pm 0.01798819\ /1.732050808$

= 0.291 ± 0.010385486

Assuming average consumption of 100 bottles (300ml) of cola drink per person, phosphorus needed in a year

2ml =1,093 mg/ml

300ml = 163.95mg/ml

Therefore in 100 bottles = 16395 mg/ml

Rough estimate Zimbabwean population is 14 000 000

14 000 000 x 16395mg/ml = 2.2953 $x10^{11}$mg/ml

DISCUSSION

The practical was generally quite well done as seen by the linear graph produced for the calibration curve hence underlying the Beer-Lambert law and this has shown that the majority of errors have been avoided during the course of the practical. This is only applicable to dilute solutions ($\leq$0,01M).Deviations at high concentration are due to changes in absorbing species or properties of bulk solution; electrical properties between molecules likely to change. The Beer's law describes the relationship between the amount of attenuation, the concentration of the absorbing species, and the path length over which absorption occurs. As light traverses absorbing analyte solution, its intensity decreases. When the solutions were in bath for 45 minutes they turned blue. The intensity of the blue colour depended on the concentration of the solution, the higher the concentration the darker the colour. Deionised water was used for dilutions because it contains no ions, therefore no ions will interact during the experiment.

However more accurate results could have been produced if the UV-vis machine was working properly.

CONCLUSION

- Concentration of P in cola sample= 546.296ppm
- Standard deviation of sample = 0.0041833
- 95% Confident limit for the sample result = 0.291 $\pm$ 0.010385486
- Amount of P needed by the Zimbabwe population assuming 100 bottles (at 300ml) of cola soft drink per person per year = 2.2953 $x10^{11}$mg/ml

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CHARACTERIZATION OF QUININE AND ITS DETERMINATION

NAME

REG NUMBER

PRAC PARTNER

COURSE

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DATE OF PRAC

TITLE : **Characterization of quinine and its determination**

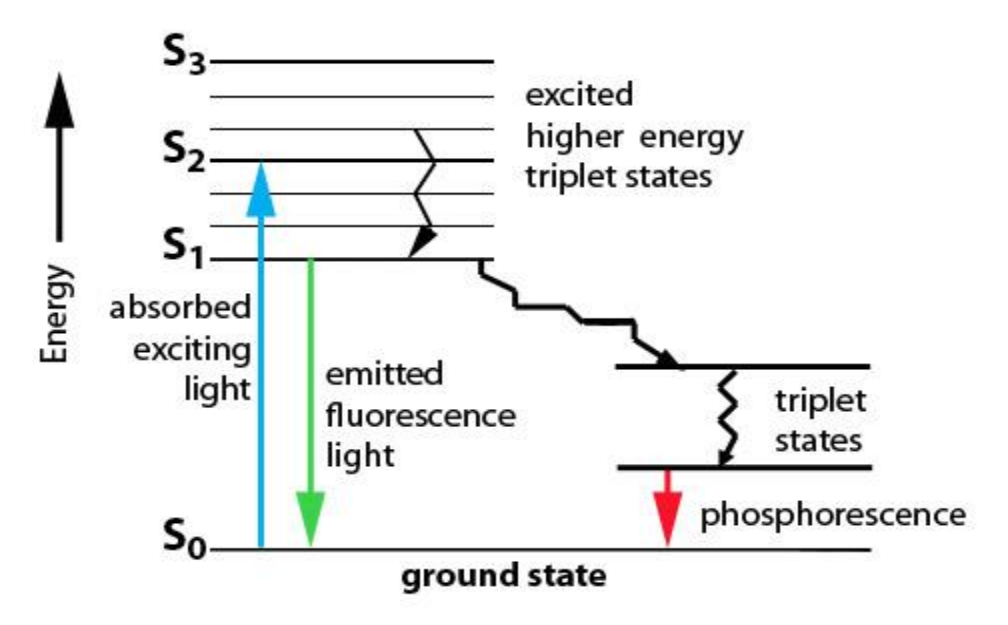
OBJECTIVES -to determine the concentration of quinine concentration in tonic water
-to determine the effect of pH dependence on fluorescence
-to determine the effect of halide quenching on fluorescence

THEORY

Fluorescence is a photoluminescence process in which atoms or molecules are excited by absorption of electromagnetic radiation. The excited species then relax to the ground state, giving up their excess energy as photons. One of the most attractive features of molecular fluorescence is its inherent sensitivity, which is often one to three orders of magnitude better than absorption spectroscopy. In fact, for selected species under controlled conditions, single molecules have been detected by fluorescence spectroscopy. Another advantage is the large linear concentration range of fluorescence methods which is significantly greater than those encountered in absorption spectroscopy. Fluorescence methods are, however much less widely applicable than absorption methods because of the relatively limited number of chemical systems that show appreciable fluorescence. (Skoog, 2009)

When radiant energy in the visible or UV portion is absorbed by a substance, electrons are raised to higher energy levels. Usually electrons return to the ground state and energy is released as heat which dissipates in the absorbing medium. With some substances, a portion of the absorbed energy is reemitted as light. If the light emission is prompt (about 10^{-8} seconds), the phenomenon is called fluorescence. The emitted light contains less energy and consequently is of longer wavelengths than the exciting light which is consistent with Stoke's Law. However, molecules give rise to band spectra rather than discrete, quantized values because of the many vibrational and rotational transitions associated with each electronic transition. Consequently, fluorescent spectra as absorbance spectra consist of connected bands and a plot of fluorescence intensity versus wavelength is often a mirror image of the absorbance curve of the same species under comparable conditions. The intensity of fluorescent light depends on various factors. For analytical purposes it suffices to state that at low concentrations (10^{-4} to 10^{-7} M) and within narrow limits, the intensity of the fluorescence is proportional both to the intensity of the exciting light and the concentration of the fluorescing species. In many cases the intensity of the fluorescence is influenced by the temperature, pH, and the presence of substances that either increase the intensity (activators) or decrease it (quenchers/ quenching agents).(Johnson, 1955)

Saturated molecules and molecules with only one double bond do not exhibit significant fluorescence. Molecules with at least one aromatic ring or multiple conjugated double bonds are prone to having fluorescence spectra in the visible region. Substituents such as OH, OCH3 and NH2 which are electron donating groups can enhance fluorescence. A plot of the fluorescence intensity vs. concentration should be linear at low concentrations. Reduction in intensity of fluorescence can be due to specific effects of constituents of the solution itself. Quenching is any reduction in intensity. Quinine has OCH3 and OH groups which are used in fluorescence. (Ewing,1995)



(Fahlman,2011)

Under usual conditions and at a concentration of about 2 μg/mL quinine, two excitation peaks (250 and 350 nm) and one emission peak (450 nm) will be seen. However, for carefully controlled conditions other peaks appear due to grating monochromator peculiarities and Rayleigh, Tyndall, and Raman scattering. Rayleigh scattering refers to radiation scattered in all directions by elastic collisions (impinging and dispersed radiation are of the same wavelength and are radiated in a random manner). In Raman scattering, the collisions are non-elastic, due to the mixing of the electromagnetic energy with the rotational and vibrational energy of the colliding molecule, and the emerging radiation will be at a different wavelength.(Harvey,2000)

There are four types of quenching which include concentration, collisional, static quenching and chemical quenching. Concentration quenching is due to absorption of fluorescent radiation by the solution. Collisional quenching is due to non-radiative loss of energy from the excited molecules. Chemical quenching is due to actual changes in the chemical nature of the fluorescent substance such as conversion of a weak acid to its anion with increasing pH. In order to separate the emitted radiation from the incident beam, fluorescence measurements are made at right angles to the incident beam. (Laitinen and Harris, 1975)

APPARATUS AND MATERIALS

1. Spectrofluorometer
2. Cuvettes
3. Volumetric Flasks
    - 1 × 1000ml
    - 6 × 100ml

- 12 × 25ml

4. Pipettes
    - 1 ml
    - 5ml
    - 10ml
5. Pippete filler
6. Spatula

PROCEDURE

A: Preparation of the Calibration Curve: Determination of Quinine in unknowns and limit of detection

A series of quinine standard solutions were prepared from a 10 µg/mL stock solution. The solutions prepared had the following concentrations 0.01, 0.05, 0.1, 0.5, and 0.8 µg/mL using 0.05M H_2SO_4 for dilutions. Fluorescence intensity of the solutions and unknown solution were determined together with H_2SO_4 blank. A sample of quinine tonic water was prepared as follows, 5 ml of tonic water were pipetted into a 250ml volumetric flask and diluted to the mark using 0.05M H_2SO_4. 5ml of this solution were pipetted into a 25 ml volumetric flask and diluted to the mark using0.05M H_2SO_4 and its fluorescence intensity was determined together with a sample of tonic water.

B: pH dependence, Quinine sulphate

2 ml of 10 µg/mL standard quinine sulphate solution were pipetted into a 25 ml volumetric flask and diluted to the mark with pH 2 buffer solution. The resultant pH of the solution was measured using a pH meter. The process was repeated using five buffer solutions between pH 3 to pH 7. The relative fluorescence intensity of the six solutions was measured.

C: Halide quenching: Quinine sulphate fluorescence

A volume of 2 ml of 10 µg/mL standard quinine sulphate solution were pipetted into a 25 ml volumetric flask and 1.0 ml of 0.05M NaBr was added and solution was diluted to the mark using 0.05M H_2SO_4. Four solutions with 2 ml of 10 µg/mL standard quinine sulphate solution were prepared in 25ml volumetric flasks and in each flask 2.0, 4.0, 8.0 and 16.0 ml portions of NaBr were added respectively. The relative fluorescence intensity of the five solutions was measured.

PREPERATION OF STOCK SOLUTIONS

Preparation of 0.05M H_2SO_4

$C_1V_1 = C_2V_2$

$5(V_1)$ =1000ml × 0.05M

V_1=10ml of H_2SO_4 was added to the 5M bench acid

Preparation of 10µg/ml quinine

$C_1V_{1=}C_2V_2$

100ppm (V_1) =10µg/ml×100ml

V_1=10ml of the 100µg was diluted to the mark of a 100ml to get the 10µg/ml

Preparation of the 0.05M NaBr

1 mole of NaBr is contained in 103g

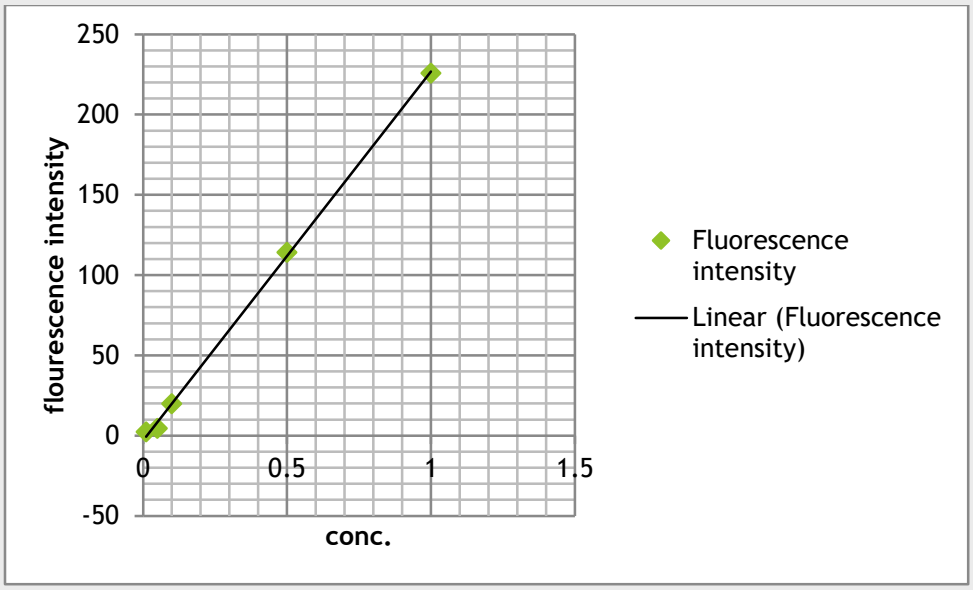
Thus 0.05 moles are contained in 0.05×103=5.15g

To make 100ml solution 0.515g of the NaBr was weighed and diluted to the mark with ionized water.

DATA

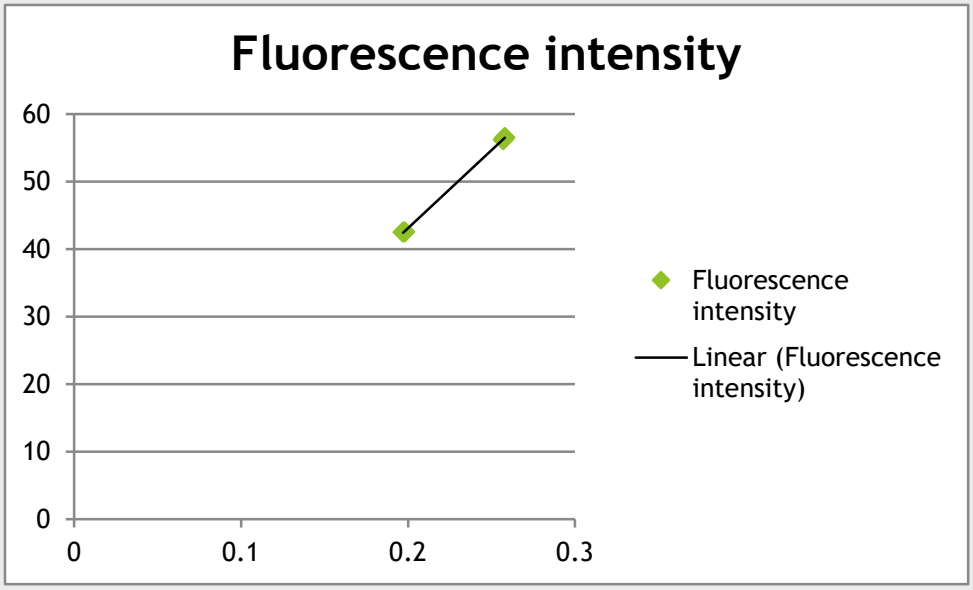
Table of relative fluorescence of quinine:

Solution	Conc./µg/ml	Fluorescence intensity
Std1	0.01	2.277
Std2	0.05	4.468
Std3	0.1	19.849
Std4	0.5	114.146
Std5	1.0	225.908



Halide quenching

solution	Concentration/µg/ml	Fluorescence intensity
001	0.257	56.184
002	0.258	56.537
003	0.197	42.501
004	0.198	42.566



ANSWERS TO QUESTIONS

1. Right angle minimizes the contributions from scattering and from the intense source radiation.

2. Other deactivation processes which compete with fluorescence are :

Vibrational Relaxation:

- It is an extremely efficient relaxation process. It is a consequence of collisions between molecules. It involves energy transfer.

Internal Conversion:

- It is highly efficient process. It is an intermolecular process.

Predissociation:

- It involves the internal conversion to higher vibrational level of lower electronic state .

Dissociation:

- No internal conversion.

External Conversion: Collisional deactivation

Intersystem Crossing: Spin flip to triple state

The final process that can compete with fluorescence is resonance energy, where the energy can be transferred without direct interaction to a second, acceptor molecule.

3.A fluorometer generates the wavelength of light required to excite the analyte of interest; it selectively transmits the wavelength of light emitted, then it measures the intensity of the emitted light. The emitted light is proportional to the concentration of the analyte being measured (up to a maximum concentration.

DISCUSSION

The plot of fluorescence intensity versus pH, it can be shown that an increase in pH leads to a decrease in fluorescence. Since fluorescence is the absorption of photons hence increase in pH is a loss of protons hence loss of that absorbed energy. The emission change of this compound arises from different number of resonance structures associated with the acidic and basic forms of the molecule. The additional resonance form provides a more stable first excited state, thus leading to fluorescence in the ultraviolet region. . This crossing and conversion of excited molecules takes place when a proton has been taken away. In quinine the groups OCH3 and OH will be affected by pH. From the plot of fluorescence intensity versus halide concentration, an increase in halide concentration decreases the fluorescence. This is due to dissolved oxygen which reduces the intensity of fluorescence in

solution and results from a photochemically induced oxidation of fluorescing species. Quenching takes place from the paramagnetic properties of molecular oxygen that promotes intersystem crossing and conversion of excited molecules to triplet state. Paramagnetic properties tend to quench fluorescence. HCL could not replace sulphuric acid because the diprotic acid is capable of providing two protons but HCL will only be able to provide one proton hence cannot compensate the fluorescing capacity of quinine. Some errors were incurred during the analysis.Since the errors in weighting a sample of a substance are usually quite small and since we completely trust those, who prepared the standard solutions the errors coming from these solutions probably can be ignored. The micropipettes used to conduct the experiment are so precise, that there as well the errors not coming from human failure can be ignored. So probably the biggest source of error is the read out of the fluorescence spectrometer. It is virtually impossible to read the values any exacter than 1 % intensity.

CONCLUSION

Fluorescence decreases as the pH of the sample increases

Fluorescence decreases as the halide ion concentration increases

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MAIN GROUP AND TRANSITION METALS CHEMISTRY
REACTION OF COPPER

NAME

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COURSE

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TITTLE REACTIONS OF COPPER

AIMS

-analyze qualitatively copper reactions
-to prepare and examine the visible

Spectra of copper complexes

THEORY

Copper has a single s electron outside the 3d shell but essentially nothing common with the alkalis except formal stoichemetries in the (I) oxidation states. The dipositive state of copper the most important oxidation state of copper, it is normally the state to which metallic copper goes upon oxidation because it much more stable when it forms complexes the copper (II) ion is stable in water and many compounds are made by metathetical reactions as well as b direct oxidation of the metal. Not only is it possible to produce a variety of compounds, but since copper (II) ion is a good complex former, numerous coordination compounds can also be obtained .Copper is widely distributed in nature as metal, in sulphides ,arsenide ,chlorides carbonates etc.It is extracted from ores ,usually by wet process, for example , by leaching and with dilute sulphuric acid ,or by solvent extraction using salycyilaldoximes and similar ligand .copper is refined by electrolysis. .(Cotton,1995)

The dipositive state of copper is by far the most important oxidation state of copper. It is normally the state to which metallic copper goes upon oxidation. Moreover, the copper (II) ion is stable in water and many compounds are made by metathetical reactions as well as b direct oxidation of the metal. Not only is it possible to produce a variety of compounds, but since copper (II) ion is a good complex former, numerous coordination compounds can also be obtained as well. (Weinberg, Argersinger and Griswold, 1960)

Since copper is a transition metals all its complexes are coloured usually blue or green .The blue or green colour is due to the presence of an absorption band in the 600 900 nm region o the absorption spectrum. The envelopes o these band are generally unsymmetrical ,seeming to encompass several overlapping transitions ,but definitive resolution into the polarised spectra of a single crystal have been measured has this resolution been achieved unambiguously. (Lee J,1996)

The pentahydrate is used as a fungicide, algaecide and herbicide. It is sometimes a precursor in the manufacture of other copper compounds and is useful as a mordant in textile dyeing and as a wood preservative. The compound is employed in a wide variety of ways, from tanning leather to toning photographs. It is available commercially in relatively high purity as a root killer for use in sewer pipes. (Phillip,1962)

Copper (II) sulfate can be produced by the reaction of the metal with hot concentrated sulphuric acid or with air and warm dilute sulfuric acid. It is commonly crystallized from solution as blue pentahydrate “blue vitriol’’ $CuSO_4.5H_2O$. Structural studies of this compound show four of the water molecules in a plane surrounding the copper atom with the fifth water moleculebeing held by hydrogen bonds to two water molecules and to oxygen atoms of two sulfate ions. As the series of lower hydrates may be obtained by moderate heating at suitable temperatures

$CuSO_4.H_2O 53 7^0C \rightarrow CuSO_4.4H_2O\ 102^0C \rightarrow CuSO_4.3H_2O\ 113^0C \rightarrow CuSO_4.H_2O$

The last water molecule can be driven off by prolonged heating between 200^0C-300^0C, yielding white anhydrous $CuSO_4$. (Huheey, 1983)

PROCEDURE A

TEST	OBSERVATION	INFERENCE
A VOLUME OF 1.3 drops of 2M NaOH were added to copper (11) sulphate solution and divided into three portions; a)solution was boiled	An insoluble blue ppt was formed Insoluble black ppt was formed	$2NaOH + CuSO_4 \rightarrow Na_2SO_4 + Cu(OH)_2$
b)A Small volume of concentrated HCl was added whilst shaking the solution	Ppt dissolves in concentrated HCl and a pale green solution is formed	$CuSO_4 + 4Cl^- + H^+ \rightarrow CuCl_4^{2-} + HSO_4^-$
c)A mass of solid NaOH was added and the mixture was warmed gently	An insoluble black ppt was formed	$Na + CuSO_4 \rightarrow NaSO_4 + Cu$
2.A piece of zinc metal was added to copper (11) solution	An insoluble black ppt was formed	$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$
3.A Volume copper (11) solution was shaken with salicylaldehyde	Immiscible droplet which sinks to the bottom	
4A granulated copper metal was added to copper (11) chloride followed by concentrated HCl, boiled for a few minutes then water was added slowly	Yellow ppt was formed	$CuCl_2 + Cl^- \rightarrow CuCl^-_3$

(B) Preparation of Bis(glycinato) Cu (ll) Hydrate

A mass of 12.5g of Cu (ll) sulphate were dissolved in 100ml of H_2O and the solution was heated to boil.This solution was added to a boiling solution of 10g of glycine dissolved in 50cm^3 of 2M NaOH. The deep blue solution was filtered hot and the obyained blue crystals were collected on a Buncher funnel,washed with a little cold H_2O ,then 25cm^3 of 96% ethanol and finally 25cm^3 of ether.The obtained sample was then dried and transferred into a stoppered sample tube.

(C) Preparation of Potassium Dioxalatocuprate (ll) dehydrate

A solution was made by dissolving 6.2g of Cu (ll) sulphate in 100cm^3 of H_2O and heated to 90º.This solution was added with vigorous stirring to a solution of 18.4g potassium oxalate in 100cm^3 of water which was at 90º.The solution was cooled to 10º in an ice water bath and the resulting solution was filtered,washed with 25ml cold water ,then with 95% ethanol and finally ether and the yield was recorded.

(D) Preparation of bis(1.2 diaminoethane) Cu (ll) sulpahate.dihydrate

A solution of 6,5g of Cu (ll) sulpahate in 50cm^3 of H_2O was added to a solution of 5cm^3 1.2-diaminoethane in 50ml of H_2O plus 50cm^3 of 96% ethanol. 200cm^3 0f 96% ethanol were added dropwise slowly with stirring to the solution from a separating funnel.The precipitated crystals were collected on a Buncher funnel and washed with ethanol and ether,air was drawn through the sample to dry it and tha yield was recorded.

RESULTS

Table 1: Weighings of copper (II) sulphate

	B	C	D
Mass of container + sample/g	100.9	94,6	94,9
Mass of container/g	88,4	88,4	88,4
Mass of sample/g	12.5	6.2	6.5

Table 2: Weighings of glycine

Mass of container + sample/g	100,4
Mass of container/g	90,4
Mass of sample/g	10.0

Table 3: Weighings of potassium oxalate

Mass of container + sample/g	106,8
Mass of container	88,4
Mass of sample/g	18.4

Table 4: Mass of Bis(glycinato) Copper (ii) hydrate

Mass of container + sample/g	101.2
Mass of container/g	88,4
Mass of sample/g	12.8

Table 5:Mass of Potassium dioxalatocupurate (ll) dehydrate

Mass of container + sample/g	96.6
Mass of container/g	88,4
Mass of sample/g	8.2

Tble 6: Mass of bis (1.2-diaminoethane**) Cu (ll) sulphate .dihydrate**

Mass of container + sample/g	97.6
Mass of container/g	88,4
Mass of sample/g	9.2

DISCUSSION

The complex bis(1.2-diaminoethane) copper (ii) sulphate hydrate failed to crystalize maybe it was because of using wrongly concentrated ethanol solutions. Complex ion formation is an equilibrium process, generally occurring in steps. Some of the species intermediate to complete coordination are relatively stable--including some precipitates. In order to insure that complexation is complete, significant excesses of ligand are advisable but here a small volume of the ligand solution was added. This might have also contributed to the failure to crystallization. The maximum absorbance of the 3 complexes that crystalized were recorded and it showed that water is a weak ligand than oxalate and glycinate ligands. A spectrochemical series is an ordering of similar complexes on the basis of splitting

energy. Remembering that $E = hc/\lambda$ for one photon of light energy (where λ is the wavelength corresponding to maximum absorbance). On the graphic trends of the positions of λmax for the complexes it showed that the glycinate complex has high splitting energy followed by oxalate and water respectively. This is because oxinate has a shorter wavelength at its maximum absorbance so the shorter the wavelength the higher the splitting energy

Crystallisation is a useful purification method for most organic compound that are solid at room temperature .The selection of a proper solvent is the most critical part of recrystallisation procedure .Adding too much solvent will prevent later recrystallisation and cause loss of product or no product at all. Low yield of bis (1,2diaminoethane) copper (II) sulphate .dihydrate and potassium dioxalatocuprate (ll) dehydrate was maybe because there was too much solvent used and only $20cm^3$ of ethanol was added and crystals did not form. In order to prevent this much more ethanol would have been used e.g. $200cm^3$ and crystals would have formed. The percentage yields of the products where low because the reaction condition did not allow maximum yield.

CONCLUSION

Mass of bis (glycinato) copper(II) hydrate was 12.8g

Mass of potassium dioxalatocupprate (II) dehydrate was 8.2g

Mass of bis (1.2 diaminoethane) Cu (ll) sulphate.dihydrate was 9.2g

λ_{max} for $CuSO_4 .5H_2O$ was 806.00nm

λ_{max} for bis (glycinato) copper (II) hydrate was 630.00nm

λ_{max} for potassium dioxalatocuprate (II) dehydrate =713.00nm

λ_{max} for bis(1,2 diaminoethane) Cu (ll)sulphate dehydrate =820.50nm

Spectrochemical series of the ligands = glycinate >oxalate >water

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D BLOCK ELEMENTS – MANGANESE

NAME:

REG #:

PROG:

DATE:

PRAC #:

TITLE: d-block elements-Manganese

AIMS: Quantitative analysis of manganese and its compounds

Preparation of manganese III compounds

To observe and draw conclusions from manganese reactions

THEORY:

After completion of the reaction ,the mixture can be freed from slid manganese(lV) oxide by filtration through glass wool, and the resulting solution evaporated until crystallisation of potassium permanganate begins.Indrustrially potassium permanganate is obtained from the potassium permanganate by oxidation with chlorine ,this reaction avoids the formation of unwanted manganese (lV) OXIDE :$2MnO_4^{2-} + Cl_2 \rightarrow 2MnO_4^- + 2Cl^-$.Powerful oxidising agents such as sodium bismuthate oxidise a solution of manganese (ll) salt to the permanganate ion ,MnO_4^-.This reaction is carried out in the presence o dilute nitric acid ,and often used as confirmatory test for manganese (ll) ions ,since the permanganate ion is intensely coloured and in very dilute solution.(Palmer,1965)

Metallic manganese is used in the manufacturing of steel, carbon steel, stainless steel, cast iron, and super alloys to increase hardness, stiffness, and strength .Manganese chloride is used in

Dyeing, disinfecting, batteries, and as a paint drier and dietary supplement. Manganese oxide (MnO) is used in textile printing, ceramics, paints, colored glass, fertilizers, and as food additives

Manganese dioxide is used in batteries and may also be generated from the welding of manganese alloys.(Weinberg, Argersinger and Griswold, 1960)

Pure manganese is obtained by the reduction of Mn_3O_4 with aluminium , followed by distillation of the manganese in vacuole. $3Mn_3O_4(s) + 8Al(s) \rightarrow 4Al_2O_3(s) + 9Mn(s)$.Reduction of MnO_2 with aluminium is dangerously explosive and this oxide is first converted into Mn_3O_4 by heating strongly in air before reduction is attempted.$3MnO_2(s) \rightarrow Mn_3O_4(s) + O_2(g)$.Most manganese is used in the form of alloys with iron, and these are obtained by reducing mixed manganese andiron ores with coke in an electric furnace. (Liptrot ,1983)

Manganese (ii) oxide occurs naturally as a brown solid and can be made by heating manganese(ii)oxide to red heat in air, it is exclusively basic. At about 1000C manganese(ii) oxide is converted into trimanganese tetroxide,Mn3O4,which contains both manganese (ii) and manganese (iii).The best known salt containing manganese in the +3 oxidation state is the fluoride,MnF3,which crystallizes as a dehydrate when manganese(ii)oxide is reacted with hydrochloric acid.In aqueous solution the Mn3+ ion is a strong oxidizing agent and readily reverts to Mn2+,it can however be stabilized by complex formation. (Durrant,1970)

Manganate (VII) is reduced to manganese(II) ion in acid solution (usually sulphuric acid):

$2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{2+} + 8H_2O + 5O_2$. In acid solution, the manganate (VII) ion is reduced to the manganese (II) ion with decolourisation. The reaction with acidified potassium manganate (VII) is used in the quantitative estimation of hydrogen peroxide. Strong oxidizing agents are required for the oxidation and amongst those commonly used are manganese(IV) oxide, MnO2, potassium dichromate(VI), K2Cr2O7, both of which need to be heated with concentrated hydrochloric acid, and potassium manganate(VII), KMnO4, which evolves chlorine at room temperature when treated with concentrated hydrochloric acid.(House J.T, 2008)

PROCEDURE :

Reactions of Manganese

TEST	OBSERVATION	INFERENCE
A 5% solution of Manganese(II) sulfate, 4M NaOH solution ($2cm^3$) was added to the test solution and allowed to stand for ten minutes	An off- white precipitate was formed , insoluble in excess Then after ten minutes a light brown precipitate was formed.	$MnSO_{4(aq)} + 2NaOH_{(aq)} \rightarrow Mn(OH)_{2(aq)} + Na_2SO_{4(aq)}$ The white precipitate was $Mn(OH)_2$ $Mn(OH)_2$ was oxidized into MnO_2 in the presence of air where MnO_2 was the light brown precipitate. $Mn(OH)_{2(aq)} + 0,5O_{2(g)} \rightarrow MnO_{2(s)} + H_2O_{(l)}$
A volume $2cm^3$ of 20 volume hydrogen peroxide was added. The precipitate was filter washed then heated with dilute HCl.	Rapid and violent reaction evolving a colorless gas which bleaches red litmus paper A dark brown ring was formed and a white ppt insoluble in excess.	$MnO_{2(aq)} + 2H_2O_{2(aq)} \rightarrow MnO^-_{4(aq)}{}^{2-} + 2H_2O_l$ $MnO_4^-aq + 4C1^-_{aq} = MnCl_{2(aq)} + C1_2g + 4H_2O_l$ manganate (VII) oxidises chloride to chlorine
A mass of KOH (1g) was dissolved in water ($3cm^3$). Manganese (IV) oxide (0,1g) was added and the suspension was heated	There was evolution of a gas that turned red litmus paper blue. A green precipitate was produced which turned to a purple precipitate.	Manganese (IV) oxide was oxidized to manganese (VI) then manganese (VII). $4KOH_{aq} + 2MnO_{2aq} + O_2 \rightarrow 2K_2MnO_{4aq} + 2H_2O_l$
Test 3 was repeated using potassium permanganate	solution turned dark purple , colorless gas evolved	$4MnO_{4(aq)}^- + 4OH_{(s)}^- \rightarrow 4MnO_{2(aq)} + 2H_2O_l + 3O_{2(g)}$

A mass of freshly prepared iron (II) sulfate solution was added in excess to $1cm^3$ of dilute potassium permanganate solution acidified with 2M H_2SO_4 and compared with a reaction which occurs when excess iron (II) sulfate was added to $1cm^3$ of potassium permanganate to which 1 drop of 2M NaOH has been added.	Potassium permanganate decolorized to give a lime green precipitate A lime green solution turned brown	$MnO_{4(aq)}^- + 8H_3O_{(aq)}^+ + 5Fe_{(aq)}^{2+} \rightarrow Mn^{2+}_{(aq)} + 5Fe^{3+}_{(aq)} + 12H_2O_l$ $MnO_{4(aq)}^- + 2OH^-_{(aq)} + 3Fe^{2+}_{(aq)} \rightarrow MnO_{2(aq)} + 4OH^-_{(aq)} + 3Fe^{3+}_{(aq)}$ Presence of MnO_2 which is brown

Preparation of manganese(iii) compound

A mass of 2.5 grams manganese(ii) was desoved in water and 7.5 grams of sodium acetate trihydrate was desolved in water.A volume of 10.5 cm^3 acetone was slowly added. The resultant 2 phase system was treated with potassium permanganate solution and after a few a few minutes a small volume was added sodium acetate solution. A stove was used to heat the solution to about 60 degrees for 10 minutes. An ice cold water bath was used to cool the solution and a filter pump was used to filter the solution.a small volume of acetone was used to dry and ice cold water was to dry.the solution was taken to the pump to dry

<u>Complementary work</u>

A small amount of the complexy was desolved in water and allowed to send for a few minutes.a note book was used to note book was used to note what happened.the coumpound was analysed and reduced using iodide.A mass of o.4 grams was added to 2M NAOH.The mixture was heated in steam water bath.A mass of 1 gram iodide was added and a volume of 25 cm^3 HCL was added.A concentration of 0.1 sodium theosulphate with starch indicator.

The maginetic suscetability was measured

RESULTS

Preparation of Manganese (III) Compound

Table 1: Weighing the mass of $MnCl_2.2H_2O$

Mass of watch glass + $MnCl_2$. $2H_2O$/g	32.5
Mass of watch glass/g	30.0
Mass of $MnCI_2.2H_2O$/g	2.5

Table 2: Weighing the mass of sodium acetate trihydrate

Mass of watch glass + sodium acetate trihydrate/g	37.5
Mass of watch glass/g	30.0
Mass of sodium acetate trihydrate/g	7. 5

Table 4: Mass of potassium permanganate.

Mass of watch glass + Manganese (III) Compound/g	30.5
Mass of watch glass/g	30.0
Mass of sample/g	0.50

Table 5 Mass of sodium acetate.

Mass of container + sample (g)	37.5
Mass of container (g)	30.0

Mass of sample (g)	7.5

Table 6: Titration with sodium thiosulphate

Final burette reading (cm^3)	38.60
Initial reading (cm^3)	23.00
Volume used (cm^3)	5.60

QUESTIONS AND CALCULATIONS

*The overall equation:

$5Mn^{2+}_{aq} + MnO_{4\,(aq)}^{-} + 15(C_5H_8O_2) \rightarrow 4H_2O_{(l)} + 7H^{+} + 5Mn(C_5H_7O_2)_{3(s)}$

From the equation potassium permanganate is the limiting reagent hence the number of moles of the product are 5 times equal to permanganate

$n(MnO_4^-)$ = mass/mr = 0.5/159 = 0.003145 moles

$n(Mn(C_5H_7O_2)$ = 5(0.003145) moles

= 0.015725 moles

therefore theoretical mass

molecular mass ×number of moles

= 352 × 0.003145

= 5.5352g

- % yield = (actual mass / theoretical mass)×100 = (2.20/5.5352)×100 = 41.1% (3s.f)
- The role $KMnO_4$ was used to oxidize the manganese (II) to manganese (III)
- Sodium acetate was used to neutralize the acid released.
- The compound has a trigonal structure bound by covalent bonds

Discussion

There are many factors affecting crystallisation, but the main ones are concentration of the solution, the time to which the solution was heated or cooled. It is important to slowly cool the flask at room temperature and then ice water. A rushed crystal formation will trap impurities within the crystal lattice. Furthermore the resulting crystals will be smaller. The yield value could have been higher, given that the crystallisation occurred in a small given time. . Do not move the flask during the crystal phase. Disturbing it can lead to the formation of small crystals and the incorporation of impurities. (B.Durrant, 1971)

A low practical yield can be thus attributed to failure of crystallization of the complex. This may have resulted from using contaminated chemicals. Mostly the chemicals used to carry out the experiments have been there for quite a long time and have been used by so many different people. Care is not really exercised in handling the chemicals say for example in the balance rooms, the same spatula used to measure to measure compound X is dipped again in compound Y without being even rinsed so the chemicals used in another practical might be in another different state or even a totally new compound as a whole if X and Y reacts.

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CONCLUSION

1. The mass of compound was 5.5352g
2. The average burette reading for thiosulphate was $5.60cm^3$
3. % yield = 41.1%
4. Theoretical mass =5.535
5. Magnetic susceptibility its magnetic

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D BLOCK ELEMENTS CHROMIUM

NAME

PROG

REG #

CORSE

Date

Title d-block elements. Chromium

Objectives : 1. to observe and explain the reactions of chromium ions.

2. To prepare compounds of chromium

a) Potassium trioxalatochromate(III) trihydrate

b) Potassium cis-dioxalatodiaquachromiate(III) dihydrate

c) Potassium trans-dioxalatodiaquachromiate(III) trihydrate

THEORY

Chromium is a member of the transition metals, in group 6. It is the first element in group 6. Chromium is a steely-grey, lustrous hard metal that takes a high polish and has a high melting point. It is also odourless, tasteless and malleable. The name of the element is derived from the Greek word "chroma", meaning colour, because many of its compounds are intensely coloured. Chromium exhibits a wide range of possible oxidation states, where the +3 state is most stable energetically. The +3 and +6 states are most commonly observed in chromium compounds, whereas the +1, +4 and +5 states are rare. Chromium (0) has an electronic configuration of 4s13d5, owing to the lower energy of the high spin configuration. (Cotton, 1972)

Aqueous solutions of Cr^{2+} ion which is sky-blue in colour are best prepared by dissolving electrolytic chromium metal in dilute mineral acids but they can also be prepared by reducing Cr3+ solutions with zinc amalgam or electrolytically. Various hydrated salts can be crystallized from these solutions an example being $CrSO_4 .5H_2O$. The Cr^{2+} ion is readily oxidised. The solutions must therefore be protected from air. Even then, they decompose at rates varying with the acidity and anions present by reducing water and liberation of hydrogen. (Phillip,1962)

Chromium exists in +4 & +6 oxidation state as CrO_2 & CrO_3 respectively where the +6 oxidation state, CrO_3 is a strong oxidizing agent that causes ignition of some organic materials. Also +6 oxidation state is acidic: $CrO_2 + H_2O \xrightarrow{} H_2CrO4$ The +4 oxidation state include those that contain the yellow chromate CrO_4^{2-} and the orange dichromate $Cr_2O_4^{2-}$ that are versatile oxidizing agents in many types of syntheses. In aqueous solutions an equilibrium exists between CrO_4^{2-} and $Cr_2O_7^{2-}$ that depends on the pHof the solution,

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

as a result basic solutions are yellow and acidic solutions are orange.

Also the outer electron configuration of chromium, $3d^54s^1$ indicates the stability of the half filled d level, $3d^54s^1$ being more stable than the expected $3d^44s^2$ for the free atom. The metal of the lower oxidation states the +3 is the most stable and common, though it can form compounds in +2, +4, +5 and +6 exists.(PALMER,1965)

Chromium (VI) ions in solution can be detected by adding an acidic H_2O_2 solution. Chromates react with hydrogen peroxide giving products in which peroxide replaces one or more oxygen atoms. In acid solution the unstable dark blue-brown chromium (VI) peroxide (CrO_5) is formed which can be stabilised as an ether adduct $CrO_5 . OR_2$.

After a few seconds the chromium (VI) peroxide decomposes to turn green as chromium (III) compounds are formed. To avoid this decomposition, it is possible to stabilise CrO5 in a water-immiscible organic solvent such as diethyl ether. (Greenwood, 1997)

The oxidation state +5 is only realised in a few compounds but are intermediates in many reactions involving oxidations by chromate. The only binary compound is the volatile chromium (V) fluoride (CrF5). It is a red solid which can be synthesised by treating chromium metal with fluorine at 400OC and 200 bar pressure. (Wollins ,1994)

PROCEDURE AND RESULTS

Table1: reactions of chromium

Test	Observation	Inference
1) NaOH was slowly added to $2cm^3$ of the test solution until in excess	dark Green precipitate which dissolved in excess sodium hydroxide	Presence of Cr^{3+} ions. $Cr^{3+}_{(aq)} + 3OH^-_{(aq)} \longrightarrow Cr(OH)_{3(s)}$ $Cr(OH)_{3(s)} + OH^-_{(aq)} \longrightarrow Cr(OH)_4^-$
2) 4M aqueous ammonia was slowly added to 2cm3 of the test solution until in excess.	grey precipitate which is insoluble in excess NH_3	Presence of Cr^{3+} ions $Cr^{3+}_{(aq)} + 3NH_{3(aq)} + 3H_2O \longrightarrow Cr(OH)_{3(s)} + 3NH^{4+}_{(aq)}$
3) $2cm^3$ of the test solution was mixed with an equal volume of 4M HCl and a little zinc dust added to it. The solution was then heated	Pale blue solution on adding 4M HCl	Cr^{3+} present: $2Cr^{3+}_{(aq)} + Zn_{(s)} \; 2Cr^{2+}_{(aq)} + Zn^{2+}_{(aq)}$ $Zn^{2+}_{(aq)} + 2HCl_{(aq)} \longrightarrow ZnCl_2 + H_{2(g)}$ Cr^{3+} is reduced by Zn to Cr^{2+}. Hydrogen is formed as a by-product of the Zn acid reaction.

		$Cr^{3+}_{(aq)} + CH_3COO^-_{(aq)}\ Cr(CH_3COO)_3$ ⟶
4) To 2cm^3 of the test solution was added a little solid ammonium peroxodisulphate. The solution was then boiled.	Light purple ppt green solution was formed on heating	Presence of Cr^{3+} ions $Cr^{3+} + NH_4(SO_4)_2$ ⟶
Test solution = 5% aqueous chromium (III) chloride		
5) 2cm^3 of the test solution were mixed with an equal volume of 4M HCl before a little zinc dust was added and the solution heated until hydrogen was evolved The test tube was then cooled and rotated to spread the solution in a thin layer over the wall.	The greyish-violet colour of the solution was replaced by a green colour on heating	Presence of Cr3+ ions $[Cr(H_2O)_6]^{3+} + Cl^-$ ⟶ $[Cr(H_2O)_5Cl]^{3+} + H_2O$
Test solution = 5% potassium dichromate		
6) A few drops of sodium hydroxide were added to the test solution	Yellow solution	Cr^{VI} present $Cr_2O_7^{2-} + 2OH^-$ ⟶ $2CrO_4^{2-} + H_2O$
Test	Observation	Inference
7) To 2cm^3 of the test solution was added an equal volume of ether. There after a solution of hydrogen peroxide was added drop wise into the solution.	Dark brown precipitation formed which then suspends	$Cr\ {}_2O_7^{2-}$ present: $Cr_2O_{7(aq)}^{2-} + H_2O_{2(aq)} + O_{2(g)}$ ⟶ $2CrO_5 + H_2O_{(aq}$
8) Test (7) was repeated with an alkaline solution	Orange solution turned yellow.	$Cr_2O_7^{2-}$ present $2Cr^{3+}_{(aq)} + 2H_2O_{2(aq)} + 10OH^-_{(aq)}$

		$\longrightarrow 2CrO_4^{2-}{}_{(aq)} + 8H_2O_{(l)}$

Table2: weighing of oxalic acid preparation of potassium trioxalatochromate(III) trihydrate

	Mass in grams
Mass of sample and watch glass	32.5 g
Mass of watch glass	23.5 g
Mass of sample	9.0 g

Table3: weighing of potassium dichromate

	Mass in grams
Mass of sample and watch glass	26.5 g
Mass of watch glass	23.5 g
Mass of sample	3.0 g

Table4: weighing of potassium oxalate

	Mass in grams
Mass of sample and watch glass	27.0 g
Mass of watch glass	23.5 g
Mass of sample	3.5 g

Table5: weighing of oxalic acid (preparation of potassium cis-dioxalatodiaquachromiate(III) dihydrate and potassium trans- dioxalatodiaquachromiate(III) trihydrate)

	Mass in grams	Mass in grams

Mass of sample and watch glass	29.2	29.2
Mass of watch glass	17.2	23.5 g
Mass of sample	12.0	12.0 g

Table6: weighing of potassium dichromate

	Mass in grams
Mass of sample and watch glass	27.5 g
Mass of watch glass	23.5 g
Mass of sample	4.0 g

Table7: weighing of potassium trioxalatochromate(III) trihydrate

	Mass in grams
Mass of sample and watch glass	29 .5 g
Mass of watch glass	23.5 g
Mass of sample	6.3 g

Table8; weighing of potassium cis-dioxalatodiaquachromiate(III) dehydrate

	Mass in grams
Mass of sample and watch glass	31.9 g
Mass of watch glass	23.5 g
Mass of sample	8.4 g

Table9: weighing of potassium trans-dioxalatodiaquachromiate(III) trihydrate

	Mass in grams
Mass of sample and watch glass	27.1g
Mass of watch glass	23.5 g
Mass of sample	3.6g

Calculations

1.Pottasium cis-dioxalatodiaquachromate (III) dihydrate

Theoretical mass

=(Mr of $K(Cr(H_2O)_2(C_2O_4)_2).2H_20$)/(Mr of $(K_2Cr_2O_7+H_2C_2O_4.2H_2O)$).16g

=(339/420).16g

=12,91g

Actual yield=12.2g

%age=(12,2/12,91).100%

=94,5%

2.Pottasium trans-dioxalatodiaquachromiate(III)trihydrate

Theoretical mass

=(Mr of $K(Cr(C_2O_4)_2(H_2O)_2).3H_2O$) =357.1

Theoretical mass =11.60357433

%age yield =16.3/11.6035733=140.4%

Discussion

The expected yield for Potassium tri-oxalato-chromate(III) is 6g. Under the microscope the crystals appear as very well formed, long, blue (monoclinic) prisms the complex salt is strongly dichroic; aqueous solutions appear blue-green to transmitted diffused daylight but magenta- coloured to transmitted artificial light. **(Palmer. G, 1954)** . The obtained yield of 6.3g was more than expected this may have been due to contamination of the crystals and water left during filtering the sample. The slightly higher yield is an indication of the impurity of the obtained crystals, maybe due to insufficient washing.

Potassium trans-dioxalatodiaquachromiate(III) trihydra

Expected Yield about 6.5g. **(Palmer G, 1954**) the obtained yield of 3.6g was far less than expected. This may have been due to several reasons. After 48hrs the solution had not reduced to about a third of the original bulk. This can be taken as an indication of having had too much of the solvent. However evaporation of the solvent may have been hindered by the fact that the crystallising dish was covered during those 48hrs therefore it is of possibility that given a few more hours the expected yield would have been achieved.

Conclusion

a) Potassium trioxalatochromate (III) trihydrate 6.0g

b) Potassium cis-dioxalatodiaquachromiate (III) dihydrate 8.4g

c) Potassium tran-dioxalatodiaquachromiate (III) trihydrate 3.6g

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D BLOCK ELEMENTS IRON

NAME

REG NO.

PROGRAM

PRACTICAL DATE

PRACTICAL NUMBER

TITLE d-block elements – Iron

AIMS AND OBJECTIVES

- To analyse the reactions of iron (11) and iron (111) compounds.
- To prepare iron (11) oxalate and potassium trioxalato ferrate (111) trihydrate.
- To analyse iron (11) for iron and oxalate.

THEORY

Mine tailings are a source of metal and non-metals contaminant. A common material in coal mines is iron pyrite. As a contaminant of coal this compound and silver compounds contribute to the production of sulphur dioxide in flue gas when coal is buried. As a material in mine tailing it contributes both iron and sulphur to water pollution when the sulfate is oxidised in a series of reaction to sulfate and the Fe (ii) oxidised to Fe (iii).

$4FeS_2 + 15O_2 + 6H_2O \rightarrow 4[Fe(OH)]_2 + 8HSO_4$.Because Fe(iii) is a strongly acidic and the net result is a dilute solution of sulphuric acid containing Fe(iii),Fe(ii) and other heavy metal irons dissolved in the acidic solution pH values of 2-3.5 have been measured.(Missler and Tarr,2007)

When iron (III) ions are added to a solution containing thiocyanate ions, a series of brilliantly red complexes form ($Fe(SCN)_3$, $Fe(SCN)_6^{3-}$, $FeSCN^{2+}$...). Thiocyanate is a sensitive test for iron (III) only- iron (II) does not cause a color change. This makes iron (II) thiocyanate useful as a quick test for the presence of peroxides and oxygen, which rapidly oxidize pale green $Fe(SCN)_2 \bullet 3H_2O$ crystals to red iron(III) thiocyanate. (Phillip, 1962)

Iron (11) oxalate, FeC_2O_4 is a lemon-coloured solid and it is of significance that its aqueous solution is yellow. Since $[Fe(H_2O)_6]^{2+}$ ions are pale green the yellow colour must be due to the presence of an iron (11) oxalate complex which is stable in aqueous solution. The following equation is suggested:

$[Fe(H_2O)_6]^{2+} + 2C_2O_4^{2-} = [Fe(C_2O_4)_2(H_2O)_2]^{2-} + 4H_2O$

Notice that the oxalate ion is bidentate i.e. each oxalate ion occupies two of the octahedral positions in the complex. Iron (11) oxalate is more correctly formulated as $Fe^{11}[Fe^{11}(C_2O_4)_2]$. (Liptrot, 1974).

The compound $K_3Fe(C_2O_4)_3.3H_2O$ can be prepared by either a metathetical reaction of ferric chloride and potassium oxalate or by the hydrogen peroxide oxidation of ferrous oxalate dihydrate (canary yellow solid, sparingly soluble in water) in the presence of excess oxalate. The compound can be crystallized as emerald green crystals. It is light sensitive but in the dark, solutions of the compound in acid medium in acid medium are stable even up to 100^0C. However when the compound is exposed to bright sunlight for and hour quantitative, photoreduction to ferrous oxalate dihydrate occurs. Oxalate content of the complex can be estimated by converting theoxalate to oxalic acid by treatment with sulphuric acid and titration with potassium permanganate at about 50-60^0C. However after photoreduction such a titration will be erroneous as both ferrous iron and oxalic acid will react with potassium permanganate.(Elias, 2002)

Both iron(II) and iron(III) ions form very stable complexes with the cyanide ion (in fact, iron is used to complex waste cyanides to render them less toxic.) The ferrocyanide ($Fe(CN)_6^{4+}$) and ferricyanide ion ($Fe(CN)_6^{3+}$) contain covalent iron-carbon bonds arranged octahedrally around the central iron. An intensely colored pigment can be made by combining these ions with iron in a different oxidation state:

$K_4Fe(CN)_6(aq) + Fe^{3+}(aq) \rightarrow KFe[Fe(CN)_6](s) + 3\ K^+(aq)$

The same pigment can be obtained from the reaction of iron (II) with ferricyanide:

$K_3Fe(CN)_6(aq) + Fe^{2+}(aq) \rightarrow KFe[Fe(CN)_6](s) + 2\ K^+(aq)$

The product of the reaction is the blue color ingredient in many artist's pigments, printing inks, and dyes (including Berlin blue, Chinese blue, mineral blue, Paris blue, and Prussian blue). The reaction is also used in blueprinting. The undeveloped paper is coated with iron (III), ferricyanide ion, and citrate. When the paper is exposed to light, the citrate reduces the iron (III) to iron(II). Moistening the paper forms the deep blue pigment. (Cotton,Wilkinson and Gauss,1995)

Reactions of iron (11) and iron (111)compounds

TABLE 1: REACTIONS OF IRON (II) AND IRON (III) COMPOUNDS

TEST	OBSERVATION	INFERENCE
An excess of 4M NaOH was added to a n iron (11) solution.	Brownish-green precipitate does not dissolve in excess.	$[Fe(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow [Fe(H_2O)_4(OH)_2]_{(aq)} + 2H_2O_{(l)}$ An aqueous solution containing iron (11) ions produces a green gelatinous precipitate of iron (11) hydroxide when a solution of alkali is added.
Reaction 1. was repeated using ammonia solution.	Green precipitate does not dissolve in excess.	$[Fe(H_2O)_6]^{2+}_{(aq)} + 2NH_{3(aq)} \longrightarrow [Fe(H_2O)_4(OH)_2]_{(aq)} + 2NH_4^+_{(aq)}$
Reaction 1. Was repeated using sodium carbonate solution.	Brownish-green precipitate does not dissolve in excess.	$FeCO_3$ precipitates as a white solid when solutions containing iron (11) ions and CO_3^{2-} ions are mixed: $Fe^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \rightarrow FeCO_{3(s)}$ Since it oxides on standing in air eventually forming iron (111) hydroxide.
Reaction 1,2 and 3 where repeated but using iron (111) solution.	1. Brown precipitate does not dissolve in excess.	

	2. Brown precipitate does not dissolve in excess. 3. Reddish-brown precipitate.	$[Fe(H_2O)_6]^{3+}_{(aq)} + NH_{3(aq)} \longrightarrow [Fe(H_2O)_3(NH_3)_3]_{(aq)}$ $[Fe(H_2O)_6]^{3+}_{(aq)} + 3CO_3^{2-}{}_{(aq)} \longrightarrow Fe(H_2O)_3(OH)_{3(s)} + 3HCO_3^{-}{}_{(aq)}$ $2Fe(H_2O)_3(OH)_{3(aq)} \longrightarrow Fe_2O_{3(s)} + 9H_2O_{(l)}$
An excess of ammonium thiocyanate solution was added to iron (11) and iron (111) solutions.	Fe^{3+}- Deep red precipitate Fe^{2+} - Red precipitate.	$[Fe(H_2O)_6]^{3+}_{(aq)} + SCN^-_{(aq)} \rightarrow [Fe(SCN)(H_2O)_5]^{2+}_{(aq)} + H_2O_{(l)}$ $[Fe(H_2O)_6]^{2+}_{(aq)} + SCN^-_{(aq)} \rightarrow [Fe(SCN)(H_2O)_5]^{3+}_{(aq)} + H_2O_{(l)}.$
Iron (111) solution from part 5 was divided into two portions and then added: (x) A little ammonium fluoride. (y) Tin (11) chloride solution.	The deep red colour disappears to leave a colourless solution. White precipitate formed on adding tin (11) chloride	
An excess of potassium iodide solution was added to an iron (111) solution followed by sodium thiosulphate solution until the mixture was colourless. A drop of ammonium thiocyanate solution was added.	Brown solution on adding KI. Decolourisation on adding thiosulphate Brown colour returned on adding thiocyanate	$2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(aq)}$ $S_2O_8^{2-}{}_{(aq)} + 2Fe^{2+}_{(aq)} \longrightarrow 2SO_4^{2-}{}_{(aq)} + 2Fe^{3+}_{(aq)}$ $2Fe^{3+}_{(aq)}$ +

3g of acetyl acetone was added to $FeCl_3.6H_2O$ (2.7g) in $20cm^3$ of water followed by sodium acetate hydrate dissolved in water. After warming for a few minutes the precipitate was filtered off and recrystallized from absolute ethanol. i. Solubility in water and diethyl ether.	Red precipitate formed Precipitate soluble in water and sparingly soluble in diethyl ether	

Preparation of iron (11) oxalate and potassium trioxalatoferrate (111) trihydrate

Table 2: Mass of iron (11) oxalate

Mass of container and compound/g	37.0
Mass of container/g	30.4
Mass of compound/g	6.6

a) Potassium trioxalatoferrate (111) trihydrate

Procedure is the same as practical schedule.

Table 3: Mass of potassium trioxalatoferrate (111) trihydrate

Mass of container and compound/g	39.4

Mass of container/g	30.4
Mass of compound/g	9.0

b) Analysis of iron (11) oxalate for iron and oxalate

Table 4:Volume of potassium permanganate used.

Final burette reading/cm3	20.00
Initial burette reading/cm3	3.00
volume used/cm3	17.00

CALCULATIONS

1) $3MnO_4^-{}_{(aq)} + 5FeC_2O_{4(aq)} + 24H^+{}_{(aq)} \longrightarrow 3Mn^{2+}{}_{(aq)} + 5Fe^{3+}{}_{(aq)} + 10CO_{2(g)} + 12H_2O_{(l)}$

No. of moles of MnO_4^- = cxv

= 0.02x(17.00/1000)

= 0.000318 moles

No. of moles of Fe = 5x0.00034

= 0.0017moles

Mass of Fe = nxMr

=0.0017 x 55.847

= 0.094g

% Fe in iron (11) oxalate = 0.094g/0.3g x 100

= 31.3%

No. of moles of oxalate = (5/3) x 0.000318

= 0.00053moles

Mass of oxalate = nxMr

= 0.00053x88.018

= 0.046g

% oxalate in iron (11) oxalate = (0.046g/0.3) x100

= 15.5%

No. of moles of water = 3:1 2

= (12/3) x 0.000318

= 0.001moles

Mass of water = 0.001molesx18.018

= 0.018g

% mass of water = (0.018/0.3)x100

= 6%

Empirical formula

Fe	$C_2O_4^{2-}$	H_2O
26.67	15.5	6
6	6	6
4	3	1

$Fe_4(C_2O_4)_3.H_2O$

2) $Fe(NH_4)_2(SO_4)_2.6H_2O_{(aq)} + H_2C_2O_4.2H_2O_{(aq)} \rightarrow FeC_2O_4(s) + H_2SO_4(aq) + (NH4)_2SO_4(aq) + 8H_20(l)$

The limiting reagent is $H_2C_2O_4.2H_2O$ thus,

Mass of oxalic acid = 7.5g

N(ammonium sulphate) = (15/388.1)

=0.0386mol

Reaction ratio of oxalic acid: product is = 1:1

n(iron (II) oxalate) = 0.0386mol

Theoretical mass = 0.0386 X 179.87

=6.95.g

% yield = (6.6/6.95) * 100

= 95%

$2Fe(C_2O_4)_{(s)} + 3K_2C_2O_{4(s)} + H2O2_{(aq)} \rightarrow 2\ K_3[Fe(C_2O_4)_3].3H_2O_{(aq)} + 3H_2O_{(l)}$

No. of moles of $3K_2C_2O_{4(s)}$ = 5g/166,2146

= 0.03moles

No. of moles of 2 $K_3[Fe(C_2O_4)_3].3H_2O$ = 3:2

=0.03×(2/3)

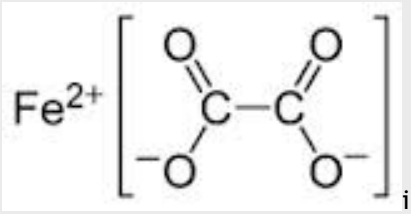
= 0.02moles

The theoretical mass = 0.02 moles×490.845

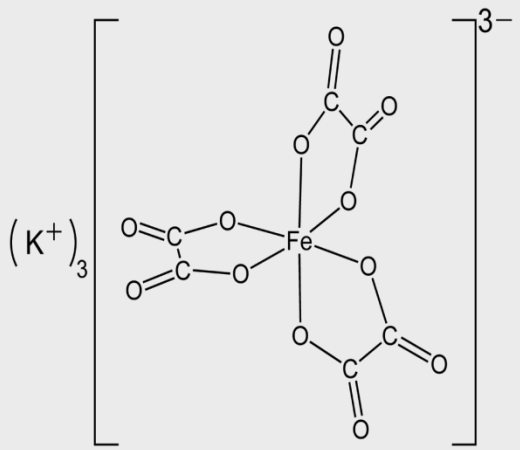
= 9.84g

The % yield = 9÷9.84g ×100

= 61%



iron 11 oxalate



3) potassium trioxalato ferrate 111

Discussion

Iron is very easily oxidised under alkaline conditions. Oxygen in the air oxidises the iron (11) hydroxide precipitate to iron (111) hydroxide especially around the top of the tube. The darkening of the precipitate comes from the same effect. (Clark, 2003)

The addition of potassium thiocyanate to a solution containing iron(III) solution is an extremely sensitive test. The test must be done under controlled conditions that is equal volumes of potassium thiocyanate are added to equal volumes o solutions containing iron(II) and suspected iron(III) ions respectively.(Liptrot,1971)

The percentage masses of the compounds in iron 11 oxalate where not equivalent to a 100% probably due to impurities because of insufficient washing of the complex to remove impurities. The bright yellow precipitate is filtered from solution, washed to remove impurities.(Granger, 2011)

A higher yield was obtained for iron (ii) compound this might be due to the presents of impurities. Grade of concentrate (crystals) has an inverse relationship with practical yield. In carrying out the practical less alcohol was used on drying and even at some point a higher yield of crystals was aimed for by using less alcohol. This resulted in some impurities which would have dissolved in alcohol crystalize affecting the yield to a higher value. So in conclusion to this it is seen that if a higher yield of solid is aimed for it means that the sample has some impurities in it. This also shows that if a better pure grade is aimed for this results in a lower yield of solids.

Conclusion

% of Fe in iron 11 oxalate = 26.67%

% of oxalate in iron 11 oxalate = 15.5%

% of water in iron 11 oxalate = 6%

Empirical formula = $Fe_4(C_2O_4)_3.H_2O$

% yield of iron II oxalate = 95%

% yield of potassium trioxalatoferrate (III) trihydrate = 61%

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THANK YOU